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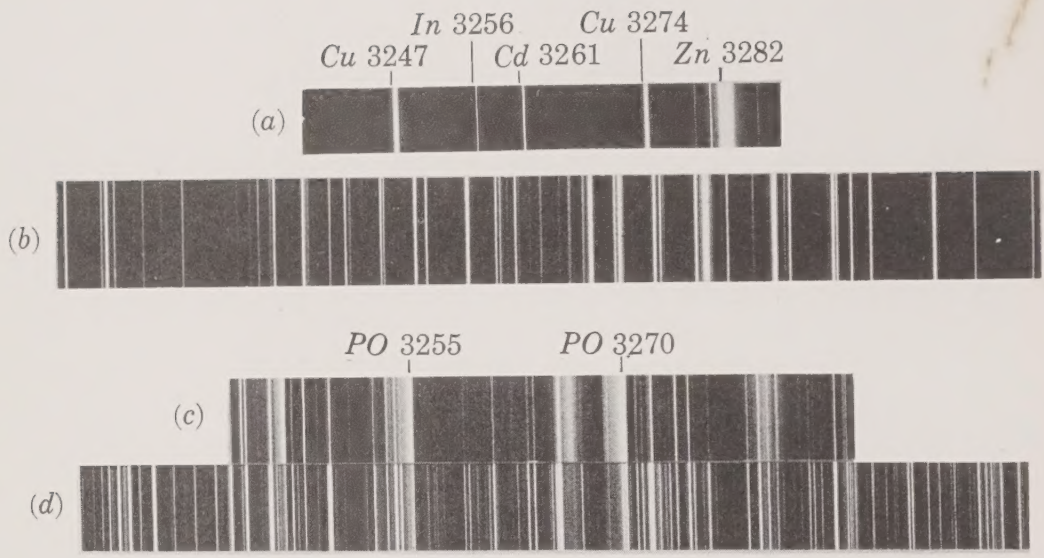

FRONTISPIECE

(a) *Simple spectrum of sphalerite.* In addition to Zn lines, sensitive lines of Cu, Cd, and In are also detectable. Each of these elements has a simple spectrum and consequently the sphalerite spectrum is simple.

(b) *Medium-complex spectrum of magnetite.* Nearly all of the lines have been emitted by iron which, since it is a transitional element, has a spectrum relatively rich in lines.

(c) *Band (molecular) spectra of monazite.* For recording these spectra cleanly, only the early period of arcing has been recorded. The bands are due to the emitter PO. Phosphorus is very volatile and after its volatilization, the rare earths and thorium volatilize strongly and cause interference (compare with (d)).

(d) *Very complex spectrum of monazite.* At this later period of arcing, the PO bands are very weak and most lines are due to the cerium earths (Ce, La, Nd, and others) and thorium. Minerals which contain several transitional elements emit extremely complex spectra and are often difficult to analyze satisfactorily.

All of the above spectra were recorded at high dispersion (2.5A/mm) and have been enlarged.

SPECTROCHEMICAL ANALYSIS

Arranged particularly for the D.C. arc analysis of minerals, rocks and soils and applicable also to ceramic materials, refractories, slag, biological ash and powders in general

By

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Foreword by

GEORGE R. HARRISON, PH.D., SC.D.

Dean of Science
Massachusetts Institute of Technology

CENTRAL FOOD TECHNOLOGICAL RESEARCH INSTITUTE * MYSORE. *
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To

E., Y., and W.

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FOREWORD

The spectroscope has long been known as one of the most powerful tools available to the scientist and the power of spectroscopic methods has been made especially evident in the determination by their use, both qualitatively and quantitatively, of the atomic species present in samples of all types of materials. The simplicity, rapidity, accuracy of identification, and more recently the precision of spectrographic emission analysis, or spectrochemical analysis as it is sometimes called, have become widely recognized during the past two decades, and no well-equipped laboratory dealing with analytical problems in agriculture, astronomy, biology, chemistry, geology, metallurgy, physics, or numerous other fields can now afford to be without spectrographic instruments.

As in other rapidly developing scientific fields, it is increasingly difficult for the user of spectrographic methods to keep abreast of new developments, especially if he does not wish to devote his full attention to them, but merely to use them as tools. So great has been the outpouring of papers on emission analysis in recent years that much duplication has resulted, and many "discoveries" and "new" methods have been reported which had previously been described in print. Now the text and reference book writers are beginning, but only beginning, to catch up with the vast amount of relevant material spread through the technical literatures of the many scientific fields in which spectrographic analysis is used.

Several excellent books which deal with the basic theory and application of spectroscopy to the analysis of materials have appeared recently, but there has been great need for a series of volumes dealing more specifically with the detailed problems that arise in analyzing samples of one given type or another. The present volume will go far toward meeting this need insofar as the mineralogist and the metallurgist are concerned; after discussing spectrochemical analysis briefly it concentrates on the special problems met with in analyzing rock ore, mineral, and soil samples, and conveniently integrates the accumulation of new lore for which a vast and rapidly growing literature must otherwise be combed.

The author of this book has for some years been in charge of the Cabot Spectrographic Laboratory, that one of the several spectroscopy laboratories of the Massachusetts Institute of Technology which is devoted to problems of mineralogical analysis, under the auspices of the Department of Geology. In the course of his extensive investigations, both in America and in South Africa, he has gained wide experience in the use of spectrographic equipment as an analytical tool in mineralogical and metallurgical

problems. This experience has fitted him admirably for the task he has set himself of bringing together in convenient form the wide and varied literature that has been built up in this phase of his subject, integrated and interpreted in the light of his wide experience.

It is hoped that this book, which will be welcomed by a wide coterie of users of the spectrograph, will be followed by others dealing with the special problems of other specialties in which spectrographic methods are useful.

GEORGE R. HARRISON.

Massachusetts Institute of Technology
Cambridge, Massachusetts
September 1950

PREFACE

In recent years spectrochemical analysis has been effectively employed to an ever-increasing extent for the analysis of a very wide variety of materials. Included in this list are minerals,* rocks, soils, ceramic materials, refractories, slag, and biological ash. These substances are grouped together here for convenience because the same general procedures can usually be applied to them all. Many papers have been written on the spectrochemical analysis of these substances. A very useful publication by Mitchell (1948),** arranged particularly for the analysis of soils, has recently been released in book form. In it the literature is reviewed exhaustively and methods of analysis that have been developed at the Macaulay Institute of Soil Research, Aberdeen (Scotland), are given in detail. There exists an urgent need for books on the analysis of the various substances which have been noted above and this book has been written in the hope that it will partly fulfill this need. It has been prepared chiefly for the analysis of minerals, rocks and soils, but much of its content applies also to the analysis of ceramic materials, refractories, slag, and biological ash. For brevity, the latter group of substances will be referred to hereafter as "related materials."

The source of excitation that has been most extensively employed for the analysis of minerals, rocks, soils, and related materials is the d.c. arc, and this book restricts itself to the use of this source. The inclusion of other sources would have produced a more cumbersome product, since each has its own characteristics and many topics (internal standardization, for example) would have to be viewed differently for each source. Furthermore, because the writer's experience has in large part been restricted to the use of the d.c. arc, he is better qualified to deal with this source.

A vital contribution to our knowledge of many of the rarer elements in the earth's crust has been made by d.c. arc analysis. Prior to the extensive application of this source, begun some twenty-five years ago, the geochemistry of many elements was imperfectly known, and abundances of several elements listed in publications at that time were in error by factors of several hundreds. Consider gallium and germanium as two examples. Twenty-five years ago their respective abundances, expressed by weight per cent, were given as 0.00000000X% and 0.000000000X%. We now

* This term includes ores, that is, those minerals used as source materials for certain elements.

** References are to bibliography at end of book.

know that the true value for gallium is 0.0015% and for germanium, 0.0007%, ± a relatively small uncertainty factor in each example. Much of our knowledge of the cosmic abundance of elements is based on d.c. arc analysis of meteoritic material. On the more practical side, the application of the d.c. arc has been vast. Industry has made extensive use of this source for the analysis of metals, alloys, source materials (ores), and various ceramic materials and refractories. In agriculture its use has been valuable for the analysis of soils and plants. In geological laboratories, the d.c. arc affords a rapid means of mineral and rock analysis; because it can be used for analysis of organic ash, it has been widely applied in biology and medicine. These are most of the major fields in which the d.c. arc has been extensively used.

Several authors who discuss sources of excitation begin with the d.c. arc, mention its simplicity and high sensitivity, and then dismiss it with a brief comment as to its suitability only for qualitative and semiquantitative analysis. To the author this has always seemed unfair, and the reputed poor reproducibility of the d.c. arc generally reflects a lack of experience with or adequate information about this simple and easily operated source. It is true that analyses with the d.c. arc are usually not quite as reproducible as with some other sources, but it can nevertheless provide quantitative results of sufficient accuracy to make the charge of semiquantitativeness unwarranted. The choice of an internal standard, however, is usually more critical than for other sources. Provided the internal standard has been carefully selected and proper attention has been given to other factors which might influence accuracy, a reproducibility (expressed as a standard deviation) of ± 5–6%, and under favorable conditions, ± 3%, should frequently be attainable.

This book has been divided into two sections. The first, based partly on a course in spectrochemical analysis given by the author in the Department of Geology at the Massachusetts Institute of Technology, covers theory, general principles, techniques of analysis, and other pertinent aspects of spectrochemical analysis. In the second section, the *spectrochemistry** of each element is discussed. *Instrumentation has in the main been omitted from this book.* Most necessary information of this type (description and discussion of spectrographic equipment) may be found in some of the general texts listed in the bibliography.

Spectrochemical analysis embraces many branches of physics, chemistry, and other sciences, and in endeavoring to maintain balance between various tangential aspects of the subject, some difficulties have been encountered.

* *Spectrochemistry* is introduced and used here as a term which embraces all those properties of an element pertinent to its analysis; for example, ease of excitation, volatilization rate, complexity of spectrum, and other characteristics.

The author has attempted to constantly bear in mind the fact that efficient qualitative and quantitative analysis of such varied and complex materials as minerals, rocks, soils, and related materials requires a judicious blending of theory and practical information, albeit the spectrograph is essentially a practical tool.

Because the very useful *Index to the Literature on Spectrochemical Analysis, Part I* (Meggers and Scribner, 1941) and *Part II* (Scribner and Meggers, 1947) which covers the years 1920–1945 is available to the spectrochemist, no attempt has been made to provide a complete bibliography here. It is understood that Part III, which will cover 1945–1950, is being prepared. Mitchell (1948) lists some 800 references, most of them pertinent to the arc spectrochemical analysis of minerals, rocks, and soils. The bibliography of a few topics not adequately covered elsewhere is given in detail here; the measurement of arc temperature is one example. A reasonably extensive bibliography on the spectrochemical analysis of each element, restricted mainly to arc methods, is provided in the second section of this book.

The discussion of the spectrochemistry of each element in the second section has been divided into short essays, each with brief resumes of some of the methods that have been employed. In the interests of brevity, all methods have not been described and, in general, details are not given. The analyst of minerals, rocks, and soils (and also ceramic materials and refractories) should attempt to include in his reading the considerable literature on the arc analysis of biological ash. The techniques are similar and much may be learned.

As an aid to the analyst, a few geochemical comments have been made on the distribution of each element. For the most part these comments are restricted to the common mineral and rock types; because of the vastness of the mineral kingdom, comments on rarer mineral and rock types are usually omitted. Use has sometimes been made of the ionic radii of elements to indicate in a general way in which minerals particular elements are likely to be found. Those not acquainted with the use of ionic radii for this purpose may consult Goldschmidt (1937a) and Rankama and Sahama (1950). Because the igneous rocks comprise a major portion of the earth's crust, a table giving the abundances of all elements in these rocks is included. The data are from the book by Rankama and Sahama (1950), which may be consulted for more detailed information on the geochemistry of the elements.

The reader may wonder how such geochemical information aids the analyst and why so much attention should be given to it. There are two good reasons. The first is that such information safeguards him from making errors of commission and omission.

> We have done those things which we ought not to have done,
> And we have left undone those things which we ought to have done
> — but there is some faith in us.

The author is painfully aware of several publications which list some elements present in minerals and rocks which are undoubtedly found only in concentrations far below detection limits. He is also aware of papers which report the absence of some *easily* detectable elements. Such errors arise from lack of information on mineral and rock composition. They have evidently been made by analysts who were not informed about the chemical composition of minerals and rocks. In defense of these errors it should be borne in mind that the spectra of many minerals and rocks are of extreme complexity.

A second reason for the inclusion of geochemical information is that the choice of an internal standard is facilitated. Without some knowledge of the geochemical distribution of the elements, the analyst will be at a loss to know which of the possible internal standards will be present in concentrations sufficient to cause interference and which will not.

The wavelength tables in the Appendix list 2–4 of the most sensitive lines of each element. These tables have been arranged in such a way that the wavelengths of all possible interfering lines (within $\pm$ 0.4–0.5A) can be easily scanned.

In the text most wavelengths are given to four figures unless there is reason to list them more precisely, in which case wavelengths are as given in the M. I. T. Wavelength Tables (Harrison, 1939). The wavelengths in the tables at the end of this book are also from the M. I. T. tables.

The author welcomes criticism on the structure of the book as a whole and on its detail. In particular, criticism on the nature and detail of the material covered in Chapters 2 and 3 would be appreciated. The lines listed in the tables as the most sensitive are correct for many elements, but for some, particularly some of the rarer elements, they must be regarded as somewhat tentative. Comments are solicited from spectrochemists on this point.

General texts on spectroscopy and spectrochemical analysis, and also books on more specific applications of spectrochemical analysis, are included in the bibliography. One of the best sources (in English) for up-to-date literature on spectrochemical analysis, is *Chemical Abstracts* (American Chemical Society). Another very useful source is the international journal, *Spectrochimica Acta*.

A periodic table of the classification of the elements is given in Appendix II.*

---

* From *Nuclear Physics*, by Francis Bitter, Addison-Wesley Press, Inc., Cambridge, Massachusetts, 1950.

ACKNOWLEDGEMENTS

Dean G. R. Harrison, who for long has been actively associated with various aspects of spectroscopy and spectrochemical analysis, has kindly written a foreword. To him very grateful acknowledgement is made for this and for his permission to use the M. I. T. Wavelength Tables for the preparation of the tables in this book. Grateful acknowledgement is also made to Dr. K. Rankama, Dr. Th. G. Sahama, and the University of Chicago Press for the use of the geochemical data in Table 7–2. A considerable portion of the material given in this book is original and much of it is due to assistants and students, in particular Mrs. L. G. Gorfinkle, Dr. W. H. Dennen, Mr. F. C. Canney, and Mr. C. Bell, who at one time or other have worked with the author in the Cabot Spectrographic Laboratory. Their ready cooperation is much appreciated. To Professor H. W. Fairbairn for continued interest and encouragement many thanks are due.

The author is deeply grateful to Professor L. Taverner, who as Director of the Government Metallurgical Laboratory, Johannesburg, encouraged the development of spectrographic research in that laboratory. During the tenure of a traveling Fellowship given by the South African Council for Scientific and Industrial Research, the author was able to continue research on spectrochemical methods, some of which has materially contributed to the preparation of this book. In the Cabot Spectrographic Laboratory, much of the research on several methods described in the book has been supported by the Office of Naval Research, Washington.

To my wife I am grateful for much needed encouragement and for proofreading.

L. H. A.

October 1950

Spectrochemical analysis has sometimes been likened unto a skilled art — this indeed it becomes when we take up the merry chase of seeking the elements in their mineral hideouts. There they often defy our probing. Their unyielding tenacity to remain hidden is then matched by all the skill and ingenuity of the analyst. Very slowly, by dint of perseverance, each — even the rarest — is made to tell the fascinating story of its distribution in the crust and waters of the earth. Those elegant little lines have done their job. Here, however, the chase never ends . . . there is evermore to be told; and so, back to work.

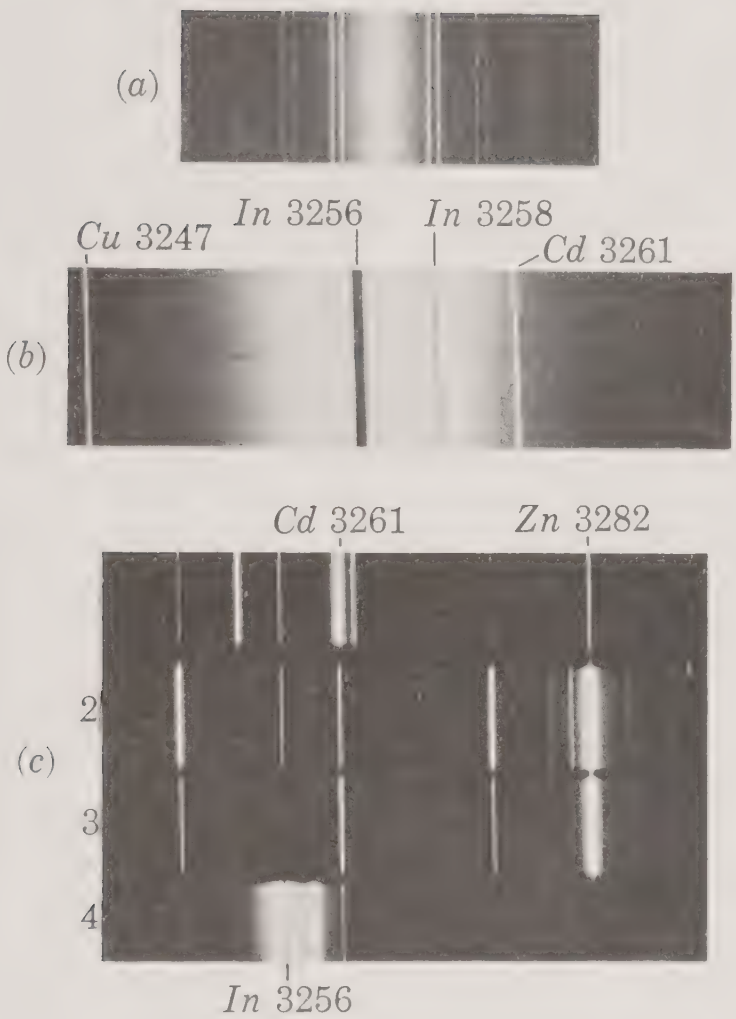

PLATE 1

(a) Rowland ghosts.
(b) Self-reversal (extreme self-absorption) in In 3256 and In 3258.
(c) Spectrum of (1) Cd salt, (2) sphalerite, light specimen, (3) sphalerite, dark specimen, (4) In salt.

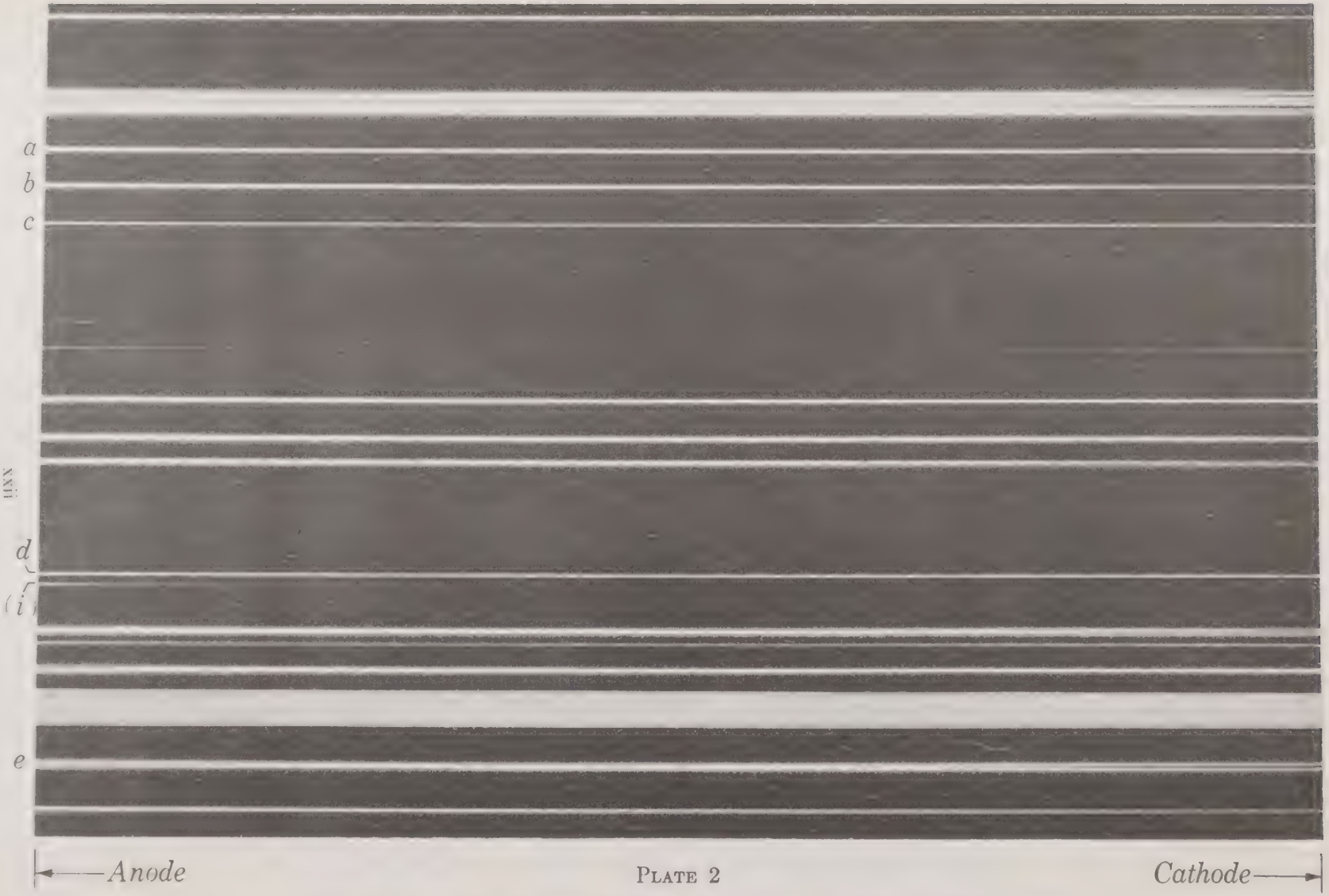

PLATE 2

Various degrees of self-absorption in iron lines, as shown by longitudinal intensity changes. (a) 3019, (b) 3017, (c) 3016, (d) 3003. The 2966 line (e) shows self-reversal near cathode. (i) is an ion line.

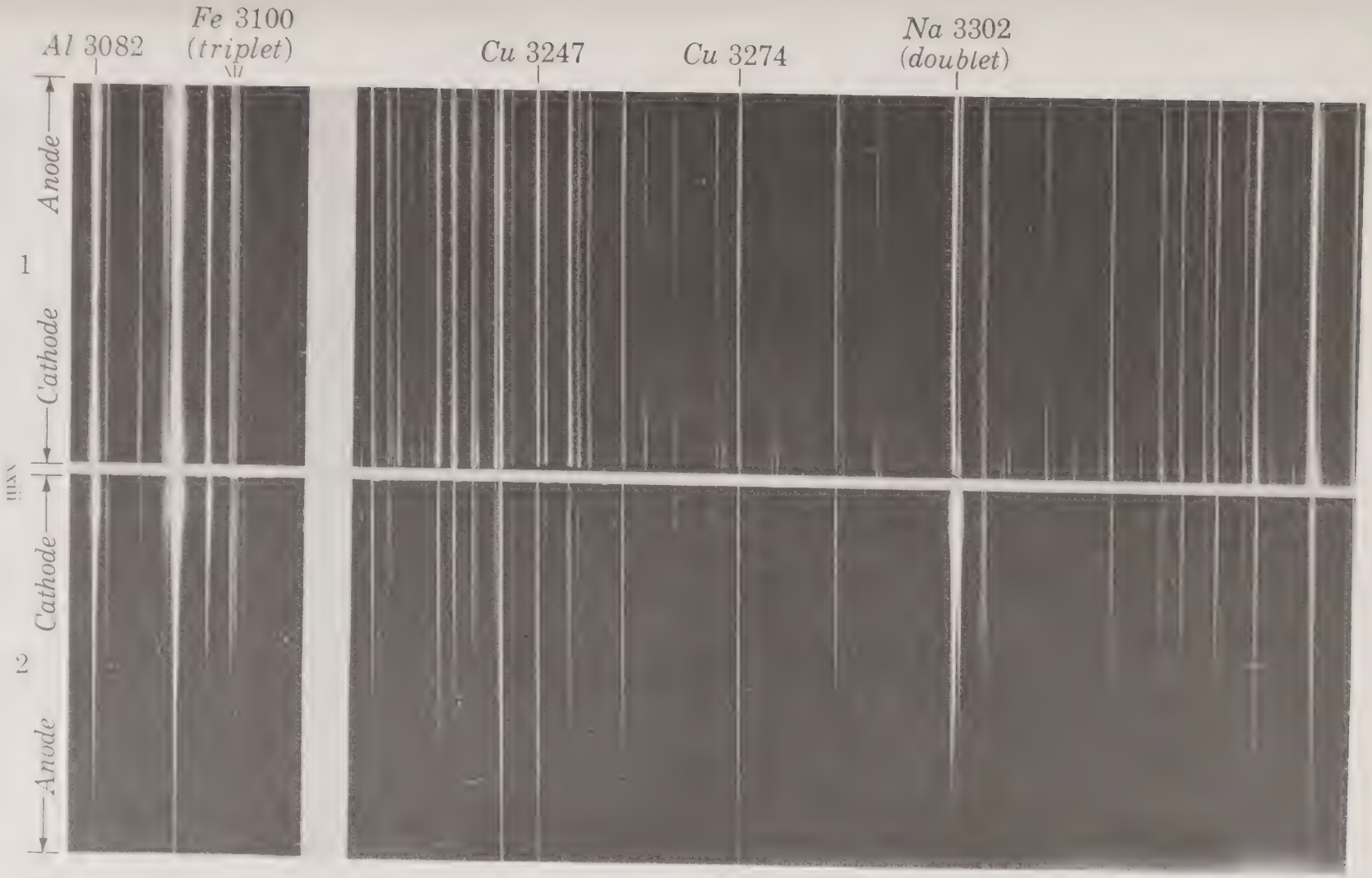

PLATE 3

Spectra emitted by a rock, showing longitudinal intensity distribution. (1) Anode excitation, (2) cathode-layer excitation.

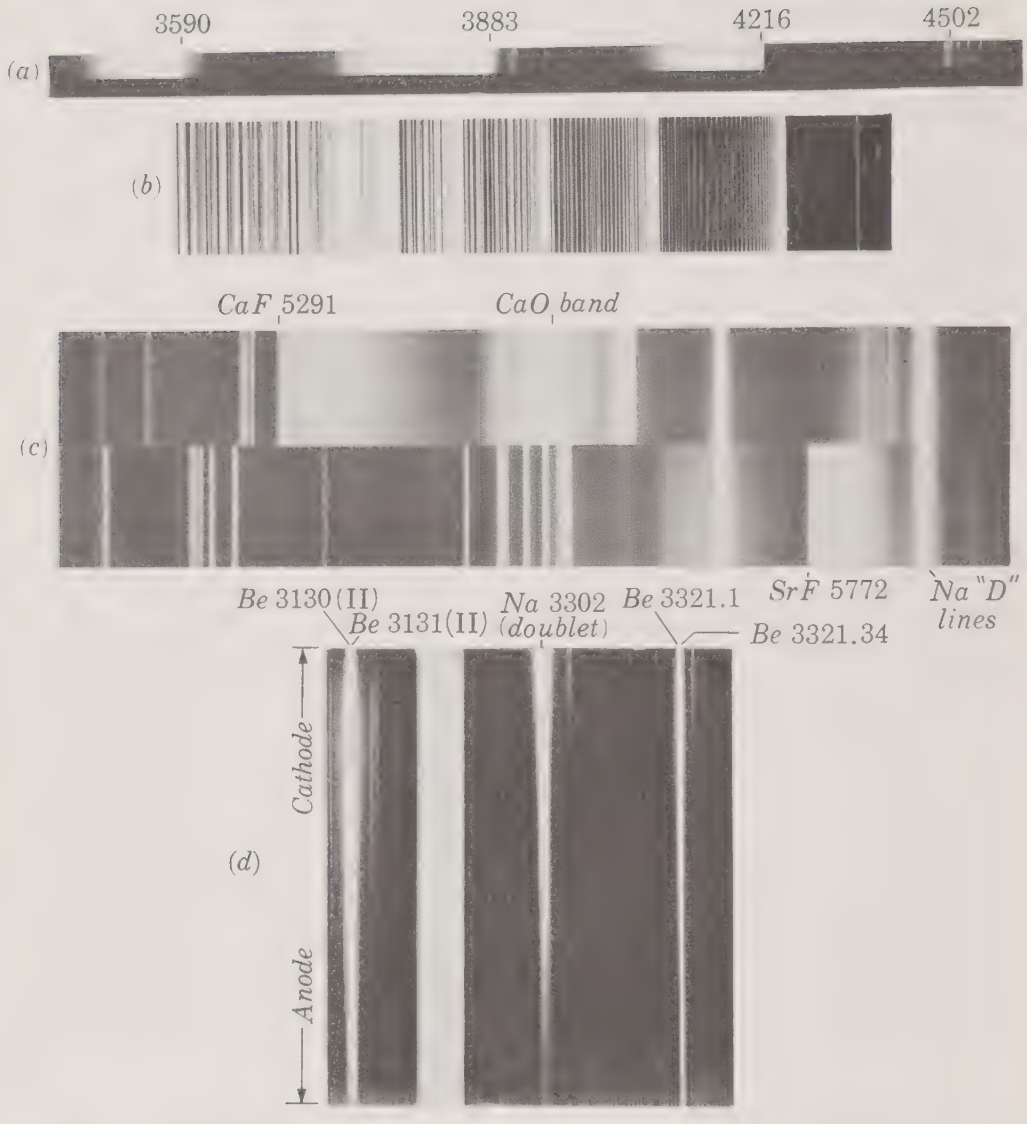

PLATE 4

(a) CN band spectra (prism optics).
(b) CN 4216. High dispersion, showing rotational fine structure.
(c) CaF and SrF bands.
(d) Longitudinal intensity distribution of Be and Na lines in cathode-layer excitation.

PART I

GENERAL PRINCIPLES

CHAPTER 1

INTRODUCTORY REMARKS

Analytical chemists now have at their disposal several methods of analysis. It is uncommon for one general method to be capable of analyzing all the elements sought, and a well-equipped laboratory will have available more than one analytical tool. This applies particularly to a laboratory handling the analysis of minerals, rocks, soils, and related materials, where a great diversity of elements is likely to be found in detectable quantities in any one specimen.

Standard chemical procedures have long provided analytical data on the major elements of minerals, rocks and soils but much attention has recently been given to the distribution and abundance of numerous rarer elements, and the call has been for methods more sensitive than the standard chemical ones. The field of colorimetry has proved fruitful and is being actively developed. Other sensitive methods — essentially methods which employ instruments developed by physicists — are also being used. These include polarographic analysis, x-ray spectrographic analysis, the use of counter devices for natural and induced radioactivity, and, finally, analysis by means of the characteristic emission spectra of the elements. This latter method has been used most widely for the analysis of the rarer constituents of minerals, rocks and soils and possesses advantages of speed and good element coverage. Furthermore, the photographed spectrum is a permanent record of analysis not only of the elements sought, but of others that may be of subsequent interest.

Spectrochemical analysis is not new and, in fact, had some early application to the qualitative analysis of minerals. It may be recalled, too, that the elements Rb, Cs, Tl, In, He, Ga, Tu, Pr, Nd, Sm, Ho, Yb, and Lu (Harrison, Lord and Loofbourow, 1948, p. 16) and A, Ne, Kr and Xe (Ramsay, 1915) were all discovered spectroscopically. Its use is also facilitating the search for radiogenic Ca^{40} (Ahrens and Evans, 1948). Only during the last two decades, however, has spectrochemical analysis been used quantitatively on a fairly large scale for the analysis of minerals, rocks, soils and related materials. This has been due in part to the stimulus given it by the Goldschmidt school of geochemistry at Göttingen in the period 1929–1936, shortly after Gerlach had introduced his principle of internal standardization, which placed accurate quantitative spectrochemical analysis on a much firmer footing. Many laboratories handling the analysis of minerals, rocks, soils, and related materials possess one or

more large spectrographs and this analytical tool is not nearly the *rara avis* it was even a decade ago.

In spectrochemical analysis atoms of an element must be energized (excited) to emit radiant energy and it is this emitted radiant energy which is analyzed in the spectrograph. As a consequence of atomic structure, each element emits its own characteristic radiant energy, or light, when excited, and after dispersal in an appropriate medium, this energy emerges in the form of a *spectrum*. When a specimen is analyzed, wavelength measurements of the component lines of its spectrum enable the analyst to ascertain which elements are present, and the brightness of these lines is a measure of the respective concentrations.

A variety of spectra emitted by minerals is shown in the frontispiece. The differences in complexity are to be noted; the spectra emitted by arcing minerals, rocks, and soils are usually complex.

A source for the purpose of exciting the elements, a narrow slit, a dispersing medium, and a device for recording the spectra are the fundamental units for spectrochemical analysis. The wavelength range of the radiant energy spectrum used in spectrochemical analysis covers 2,000–9,000A, where 1A (Angstrom) = 10^{-8} cm. On rare occasions longer or shorter wavelengths may be used.

Hot flames (for example, oxyacetylene), arcs (d.c. and high voltage a.c.), and sparks are most commonly used for the excitation of an element. Flames possess the lowest energy of excitation, and in them the maximum attainable temperature is about 3,000° C. They are capable of exciting some thirty elements, namely, Ag, Au, Ba, Ca, Cd, Co, Cr, Cs, Cu, Dy, Fe, Ga, Gd, Hg, In, K, La, Li, Mg, Mn, Na, Nd, Ni, Pb, Pd, Pr, Rb, Rh, Ru, Sc, Sr, Tl, Y, and Zn. As a source of excitation the flame is, therefore, somewhat restricted in its application. It has frequently been used in soil analyses (Lundegardh, 1929 and 1934; Mitchell, 1948) and sometimes for mineral and rock analyses.

The d.c. arc is a more energetic source of excitation than the flame and has been widely used for the analysis of minerals, rocks, soils, and related materials. By means of the d.c. arc it is possible to excite appreciably some seventy elements, in addition to the molecular emitters CaF and SrF, by means of which fluorine can be analyzed. Mitchell (1948) lists the following elements as capable of analysis in the d.c. arc: Ag, Al, As, Au, B, Ba, Be, Bi, C, Ca, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, F, Fe, Ga, Gd, Ge, Hf, Hg, Ho, In, Ir, K, La, Li, Lu, Mg, Mn, Mo, Na, Nb (Cb), Nd, Ni, Os, P, Pb, Pd, Pr, Pt, Ra, Rb, Re, Rh, Ru, Sb, Sc, Si, Sm, Sn, Sr, Ta, Tb, Te, Th, Ti, Tl, Tm, U, V, W, Y, Yb, Zn, and Zr.

The highest energy of excitation is attained in the spark source. In this source elements difficult to excite may be energized (the halogens and

noble gases for example). The spark is in general, however, not as easily adapted to the analysis of minerals, rocks, soils, and related materials as the arc. A spark solution technique may be used for a mineral analysis by passing spark discharge through a solution obtained from a mineral. Considerable use has been made of such excitation of mineral solutions at the Freiburg Mineralogical Institute, Freiburg, where methods developed particularly by H. Moritz and F. Leutwein are employed. See for example a publication by Schneiderhöhn *et al* (1949) which gives the analyses of several elements (notably Ti, V, Cr, Mo, Mn, Ni and sometimes others) in various sedimentary rock types. This publication refers to other publications from the Freiburg Institute on the use of spark excitation of solutions. The copper spark method of Fred, Nachtrieb and Tomkins (1947) holds promise for direct spark excitation of minerals, rocks, and soils. Because of its high reproducibility, much use has been made of the spark source for the quantitative analysis of metals and alloys.

The high-voltage a.c. arc has sometimes been used for mineral analyses; see for example Rennhackkamp (1949).

The prism is a common dispersing medium, and in it refraction of radiant energy varies with wavelength; red light (radiation of relatively long wavelength) is refracted less than blue light (radiation of relatively short wavelength). Dispersal may also be obtained by means of diffraction in a grating; here red light is diffracted more than blue light.

Prisms are usually of quartz or glass. If the ultraviolet region is to be used for analysis, quartz optics are necessary, as glass absorbs radiation of wavelength shorter than about 3,500A. At relatively high wavelengths, dispersion by a quartz prism becomes very small, and a glass prism is frequently employed if complex spectra are to be analyzed. Some prism spectrographs (for example, the large Littrow models by Adam Hilger, London) have interchangeable glass and quartz prisms. Although the spectra of some few minerals, such as *sphalerite*, *cassiterite*, and *galena*, are relatively simple, very complex spectra are emitted by a majority of minerals and soils, and by nearly all rocks, and the largest prism instruments must be used to attain sufficient dispersion.

Although the spectra emitted by minerals and rocks are complex, the largest *grating* spectrographs are not recommended for analytical laboratories. By their use linear dispersions* of 0.5–1.0 A/mm may be attainable in the first order spectrum. These dispersions are, however, wasteful of

* As defined by physicists, linear dispersion = $dl/d\lambda$, where dl is the distance of separation of two closely spaced lines differing in wavelength by $d\lambda$. In spectrochemical analysis it has, however, become common to use the reciprocal of linear dispersion (sometimes also known as the plate factor) and refer to this as the *dispersion*. This is expressed in A/mm.

plate space. Very large grating instruments have their use in a physics laboratory where, for example, they could be utilized for an examination of the fine structure in molecular spectra. For general analytical work on minerals, rocks, and related materials, a linear dispersion of 2.5–7.0 A/mm is recommended.

For the analysis of the complex spectra emitted by minerals, rocks, and soils, not only is a good dispersion required, but *resolving power* should be high. Resolving power is a measure of the ability of a spectrograph to resolve two closely spaced lines of about equal intensity and is defined as $\lambda/d\lambda$, where $d\lambda$ is the wavelength difference between the two lines. The resolving powers of most spectrographs fall within 5,000–20,000. See Harrison, Lord, and Loofbourow (1948, Chapter 2) for a more detailed discussion on resolving power and dispersion and their relationship.

Because of a marked increase in the production of good gratings, many spectrographs are now of this type, particularly in the United States. A grating is produced by ruling lines (actually grooves) at extremely close intervals (for example, 15,000 lines per inch) on a highly polished surface such as evaporated aluminum on glass.

The three major criticisms of grating spectrographs are (1) possible misidentification of lines because of the presence of ghost lines; (2) possible misidentification of lines because of overlapping of orders, and (3) variable reflectivity at different wavelengths.

(1) Ghosts are of two types. Plate 1 shows typical Rowland ghosts, due to overexposure of the Be doublet, Be 3131.072 and Be 3130.416. Because of the symmetrical disposition of these ghost lines about the parent line, they can usually be recognized quite easily. In good gratings, such ghosts will have an intensity of less than about 0.1% of the parent line and are thus found grouped only about heavily exposed lines. Greater difficulty may be encountered from the presence of Lyman ghosts. These are usually much weaker than Rowland ghosts and are not so easily recognized. See Harrison, Lord, and Loofbourow (1948, p. 44 and p. 100) for discussion of ghosts and their detection.

(2) In practice, misidentification of lines due to overlapping of orders has been found to be very nearly negligible; an experienced analyst should not commit an error of this type.

(3) Variable reflectivity in gratings may cause difficulty. Some gratings have poor reflectivity ("holes") at certain wavelengths. This may be serious in a mineral, rock, or soil analysis because frequently several elements are sought at very low concentrations. Some of these may become undetectable in a particular spectrograph if the wavelengths of their sensitive lines correspond to a "hole" in the grating. Analysts are not

aware of this unless they have worked with both prism and grating spectrographs.

One real advantage of a grating spectrograph is constancy of dispersion at all wavelengths. As a result line identification is much simpler than in prism spectrographs and the excessive crowding of lines at long wavelengths is absent. The author's experience with both types inclines him slightly in favor of the grating spectrograph, provided there is the assurance that the grating is of first class quality in all respects. Further comments on the grating vs. prism discussion will not be made here; suffice it to say that good analyses of minerals, rocks, soils, and related materials may be made with either instrument. See Slavin (1940b), Twyman (1941), Harrison (1938), Harrison, Lord and Loofbourow (1948), and Hilger and Watts and Jarrell-Ash (1950) for further reading on the prism vs. grating discussion.

Early spectrochemists observed spectra visually but this method has been largely replaced by permanent photographic records. Visual inspection of spectra is limited to that wavelength range to which the eye is sensitive, namely, about 3600A–8000A. Further, a visual analysis would be particularly awkward in many mineral, rock, or soil analyses because of the complexity of the spectra. Visual analysis using the arc source, however, sometimes finds considerable use for the rapid, qualitative analysis of minerals (Section 5–11). Electronic devices have recently been developed for recording the presence and intensity of spectral lines. These methods are extraordinarily rapid but instrumentation is very complex and expensive. Electronic recording is suitable only for the routine analysis of a relatively few constituents in metals and alloys. At present its general use in a mineral, rock, or soil analysis is impractical. When spectra are recorded photographically, plate or film may be used, although the former is generally preferred.

As details about spectrographic instrumentation are considered beyond the scope of this book, reference may be made to Sawyer (1944), Brode (1945), and particularly Harrison, Lord, and Loofbourow (1948). General spectroscopy is covered in these three books and they contain some chapters on spectrochemical analysis.

For a general introduction to spectrochemical analysis the reader may refer to Meggers (1946), who gives a readable account both of historical perspective and fundamental principles of the subject.

CHAPTER 2

THE ORIGIN AND INTERPRETATION OF SPECTRA

2–1. Introduction. To some spectrochemists, the inclusion of a chapter on the theory of atomic spectra may be felt to be superfluous in a book written for analytical purposes only. To many analysts, however, it has become clear that a lack of theoretical background on the purely physical aspects of line spectra is a handicap, particularly in the development of accurate quantitative methods. A fair proportion of analysts have tended to consider *en masse* all the lines emitted by an element and frequently, therefore, have been unable to appreciate properly the interesting and significant individuality of each spectrum line, that is, its distinctive energy characteristics. A perusal of papers on spectrochemical analysis leads one to conclude that many analysts lack sufficient theoretical background and this has prompted Meggers (1946) to state, "Unfortunately, very little use appears to be made of excitation data in spectrochemical analysis, except in astrophysics. An indication that this is true is seen in the infrequent mention of excitation potentials in spectrochemical literature."

It is true, of course, that spectrochemists who analyze minerals, rocks, soils, and allied materials have usually had very different academic trainings — some are physicists, some chemists, some geologists; a few are engineers. Many physicists and some chemists will have had sufficient theory, but for most geologists and engineers this background will be lacking.

The author hopes that the treatment given in this chapter, although elementary, will meet the requirements of the practicing spectrochemist. It should serve to acquaint him with spectroscopic notation, and particularly aid him to obtain excitation data on the lines used for analysis and thereby enable him to utilize them with maximum proficiency.

2–2. Atomic structure and quantum theory. The atom of any element consists of a small, compact nucleus made up of protons and neutrons and surrounded by one or more orbital electrons. Each electron carries a negative charge equal and opposite in sign to that of the protons, whereas neutrons are electrically neutral. The number of protons equals the number of electrons in neutral atoms and this number, the atomic number Z, is characteristic of each element. Orbital electrons are not haphazardly distributed about the nucleus but may be considered as located in orbits,

with which are associated discrete energies. Each orbit may be regarded as corresponding to an *energy level* in the atom.

The newer wave-mechanical treatment of electronic structure has tended to replace the simpler so-called Bohr orbits with electron clouds which are rather difficult to visualize. For our purpose, however, it is simpler and quite as satisfactory to retain the atomic model of electronic orbits.

To explain satisfactorily the emission of radiant energy, Planck introduced the quantum theory. This theory postulated that radiant energy is emitted discontinuously in integral multiples of a fundamental unit, called a *quantum*, and that the energy, e, of a quantum is proportional to the frequency of the emitted light, or radiant energy. Thus,

$$e = h\nu, \tag{2–1}$$

where h is Planck's constant (6.62×10^{-27} erg-second) and ν is the frequency of the radiation in vibrations per second. The quantum theory has had one of its greatest successes in the interpretation of spectra.

When an atom is undisturbed all electrons occupy orbits (energy levels) of lowest energy; in this condition the atom is said to be in the *ground state*. If an atom is excited by violent collision with a fast-moving particle (atom, ion, molecule, or electron), the more loosely held outer (valence) electrons shoot out to higher energy levels (orbits farther removed from the nucleus). This condition is an unstable one and when each electron returns to its original orbit, radiant energy is emitted in the form of quanta which produce spectral lines. Each electron can return to its original location by one "jump," or it may return in a series of "jumps" via intermediate energy levels. In the former instance one spectral line would be emitted, and in the latter, several. The energy of any line of the emitted radiation, that is, the energy difference between the two levels involved, is given, in accordance with Bohr's application of the quantum theory of radiation to spectroscopy, by

$$E_2 - E_1 = e = h\nu, \tag{2–2}$$

where E_2 is the energy of the higher level and E_1 that of the lower. In place of frequency, spectroscopists usually employ ν' (wave number) and the relationship between ν, ν', and λ (wavelength) is

$$\begin{cases} \dfrac{1}{\lambda} = \nu' = \dfrac{\nu}{c}; \\ \lambda\nu = c \text{ and } \lambda\nu' = 1, \end{cases} \tag{2–3}$$

where c is the velocity of light (3.0×10^{10} cm per second). The unit for ν' is cm^{-1} (waves per centimeter).

By applying the quantum theory to the interpretation of the radiant energy spectrum, it is possible to show that for the simplest element, hydrogen, the ν' of a line is given by

$$\nu' = \frac{1}{hc}(E_2 - E_1) = R\left(\frac{1}{I^2} - \frac{1}{n^2}\right), \tag{2–4}$$

where R is a fundamental constant (the Rydberg constant, 109,678 cm^{-1}, the value of which was obtained by calculation), I is a constant and is integral, and n may have integral values $> I$.

Early in the history of spectroscopy (1885), Balmer had measured the wave numbers of a group of lines (a *series*) of the visible hydrogen spectrum and found that the wave number of each line in this series (the Balmer series) could be represented by a difference of two terms, thus,

$$\nu' = \frac{R}{I^2} - \frac{R}{n^2}, \tag{2–5}$$

where R is a constant equal in value to R in Eq. (2–4), $I = 2$, and $n = 3, 4, 5, 6. \ldots$ Other series of lines in the hydrogen spectrum were discovered and in each instance the wave number of a line in the series could be expressed by the difference of two terms, as in Eq. (2–5). For each series I is a constant and $n > I$.

Like hydrogen, each element has different series of spectra and in each series it is possible to express the wave number of any line as a difference of two terms. Eq. (2–5) may be rewritten in the general form,

$$\nu' = L - \frac{R}{(n - a)^2}, \tag{2–6}$$

where L is the convergence limit for any series obtained by putting n equal to infinity; a is approximately constant for any series.

The agreement between Eq. (2–5) and Eq. (2–4) is remarkable and the values of R obtained by actual measurement of line wavelengths in a series and by application of the quantum theory are amazingly close. This accurate interpretation of the emission of spectral lines has led to the complete acceptance of the fundamental postulates of the quantum theory given at the beginning of this chapter. The older *terms* of the early spectroscopists refer therefore to *energy levels* in the atom.

2–3. Quantum numbers. To interpret the emission of spectral lines according to the quantum theory, it has been necessary to introduce *quantum numbers*.

In its orbit, the distance of an electron from the nucleus may be regarded as associated with the *principal quantum number*, n, which is an integer and can have values of 0, 1, 2, 3, 4. . . . The angular momentum of an electron in its orbit is associated with the *orbital* quantum number, l, which can have integral values from 0 to $n - 1$. Spectroscopic symbols have been introduced for different values of l, as follows:

$$l = 0, 1, 2, 3, 4, 5, \ldots$$
$$\text{symbol } s, p, d, f, g, h, \ldots$$

The value of l determines the shape of an orbit. For a given value of n, a minimum value of l indicates greatest eccentricity and a maximum value, a circular orbit.

In the early development of spectroscopy, it was found that, except for the simplest of atoms, four different series of lines could be distinguished: these were named Principal, Sharp, Diffuse, and Fundamental. The names Sharp and Diffuse do have some significance in describing the nature of lines in the respective series, but Principal and Fundamental are meaningless from a descriptive aspect; their usage has been retained, however, because their initial letters (S, P, D, and F) are employed to distinguish line series.

The value of l determines the series to which a given line will belong:

Lines of the Principal series involve $s-p$ transitions,
Lines of the Sharp series involve $p-s$ transitions,
Lines of the Diffuse series involve $p-d$ transitions,
Lines of the Fundamental series involve $d-f$ transitions.

It is therefore possible to classify the spectrum of an element into broad groups (series) according to the l values of the electron involved in excitation.

Another quantum number, the *spin quantum number*, is discussed under "Multiplicity."

2–4. Multiplicity. If a spectrograph of large dispersion is used, many lines that appeared as single lines under small dispersion reveal themselves to be made up of several components. These line groups are referred to as *multiplets*.

Multiplet structure of spectral lines has been interpreted by introducing the concept of spin and the spin quantum number, s; for each electron s may equal $+\frac{1}{2}$ or $-\frac{1}{2}$.

The multiplicity, M, of the lines of an element is given by

$$M = 2S + 1,$$

where S* is the *sum* of the individual spins (s) for each electron in the atom. Because in ordinary excitation only outer (valence) electrons are involved, the value of S, and hence of M, will depend only on the spin of these electrons. Consider an element with one outer electron; s can equal either $+\frac{1}{2}$ or $-\frac{1}{2}$. As there is only a difference of sign, $S = \frac{1}{2}$, $M = 2$, and a doublet spectrum is produced. This is found true of elements such as the alkali metals, which have one electron outside closed shells.

* This S, a quantum number, is not to be confused with S, the symbol for $L = 0$ (page 11).

For the alkaline earths, two electrons are present, each of which can have spin values of $+\frac{1}{2}$ or $-\frac{1}{2}$. The following spin value combinations are possible for the two electrons:

$+\frac{1}{2}$ and $+\frac{1}{2} = 1$ $\quad$ $-\frac{1}{2}$ and $+\frac{1}{2} = 0$
$-\frac{1}{2}$ and $-\frac{1}{2} = 1$ $\quad$ $+\frac{1}{2}$ and $-\frac{1}{2} = 0$

S can therefore equal 1 or 0 and M, 3 or 1. Triplets and singlets are thus characteristic of the spectra of the alkaline earths.

Possible multiplicities for different numbers of electrons involved in excitation are given in Table 2–1.

TABLE 2–1

Number of electrons	*Possible multiplicities*
1	Doublets
2	Singlets, triplets
3	Doublets, quartets
4	Singlets, triplets, quintets
5	Doublets, quartets, sextets

From Table 2–1, it is evident that even multiplicities are found in the spectra of elements which have an odd number of emission electrons and odd multiplicities are found in the spectra of elements having an even number of emission electrons.

The complexity of a spectrum increases as more electrons are involved in excitation and because the transitional elements have several labile electrons which are easily excited, their spectra are highly complex. Many minerals contain several transitional elements and their spectra are extremely complex; minerals containing several rare earths have probably the worst crowding of lines and their successful analysis often poses a serious problem.

Although the *number* of line components in a multiplet is determined by the vlaue of S, the frequency (ν) of each line is not determined by the value of S alone. To interpret this splitting of energy levels, a quantum number J, sometimes referred to as an *inner quantum number*, is introduced.* (See Section 2–5.)

* In perusing books on spectroscopy, the reader may find mention of another quantum number, the *magnetic quantum number m*. This quantum number has been introduced to explain a very fine splitting of apparently single lines which results from a small splitting of energy levels in a powerful magnetic field. Also, by using m, as well as the quantum numbers n, l, and s, it has been possible to classify and arrange the elements in the Periodic Table with the aid of the *Pauli exclusion principle*. Since in spectrochemical analysis we have to consider only the energy states of the atom as involved in excitation from an ordinary source,

2–5. Energy levels (states) of an atom. Analogous to the use of S, the *total* spin quantum number, L, is used as the symbol for the total orbital angular momentum for all electrons in the atom as a whole. Whereas the symbols s, p, d, f are employed for values of 0, 1, 2, and 3 for individual electrons, S, P, D, F are the corresponding L-values for $L = 0$, 1, 2, and 3,

The total energy associated with a given level or state of an atom depends on S and L, and also on the interaction or coupling of S and L. This coupling gives a total angular momentum for the atom and is called J. the inner quantum number. J can have all values of $L + S \ldots L - S$. The multiplet structures in different line series are dependent on J-values.

A given energy level is symbolized as

$$n^M L_J,$$

which is commonly known as a *term symbol;* n is the principal quantum number and M, L, and J are the symbols for multiplicity, total orbital quantum number, and inner quantum number, respectively. Sometimes n is omitted in writing the term symbol.

As the emission of a spectral line involves an electron "jump" between two energy levels, each line may be classified by two term symbols, one for the lower energy level and one for the upper energy level. Consider the two sodium D lines, Na 5895 and Na 5889. The low state is common to both and this level has $n = 3$, $L = 0 = S$; S (spin) $= \frac{1}{2}$, and hence $M = 2$; $J = \frac{1}{2}$. The upper state has $n = 3$, $L = 1 = P$; for 5889, $J = 3/2$ and for 5895, $J = \frac{1}{2}$. The two levels for each line may be represented by the symbols,

$$\text{Na } 5889\text{: } 3\,^2S_{1/2} - 3\,^2P_{3/2}$$
$$\text{Na } 5895\text{: } 3\,^2S_{1/2} - 3\,^2P_{1/2}$$

The term symbol of the lower level ($3\,^2S_{1/2}$ in this example) is usually written first.

Using term symbols as above, it is possible to classify all lines in a spectrum; each line is classified according to its lower and upper energy levels.

2–6. Some selection rules. Energy level transitions are governed by certain selection rules. ΔL can either $= 0$ or ± 1, and not 2 or more. Thus, for example, S-P, S-S, D-P transitions are permissible but not S-D or P-F. Likewise $J = 0$ or ± 1, with the restriction that ΔJ does not equal 0, when $J = 0$.

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and not extremely fine splitting of levels in a huge magnetic field, m is not considered in the normal symbol assignment of energy levels (page 11) and need not therefore be considered here.

2–7. Graphical representation of energy levels or terms: Excitation potentials. The energy transitions involved in the production of spectra may be depicted graphically by means of a *Grotrian energy level diagram*, which is shown for the gold atom in Fig. 2–1 (after Grotrian, 1928). The ordinates are energy scales, and energy levels are drawn as horizontal lines. The energy scale at right is given in cm^{-1} and that on the left is a volt scale, beginning with the ground state as = 0. This volt scale may be used directly to obtain the *excitation potential* of a line, which is a measure of the energy required to excite an atom to emit the line and is commonly expressed in *electron volts*. One electron volt is equivalent to the energy acquired by an electron after it has been accelerated by a potential difference of one volt. Wavelengths and wave numbers can be converted to electron volts by use of the conversion factor, 1 volt = 8067 cm^{-1}.

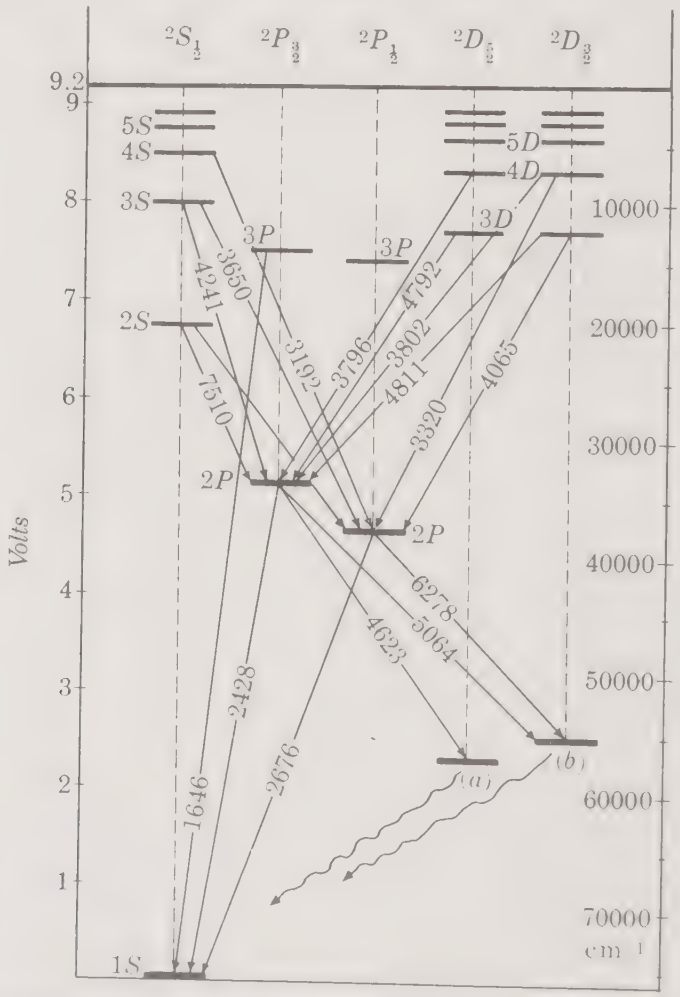

Fig. 2–1. Grotrian energy level diagram for the gold atom. The wiggly arrows indicate a transition that is forbidden by the selection rules (Section 2–6).

The height of the upper level of a given line above the ground state (= 0 volts) is its excitation potential; thus from Fig. 2-1 it can be seen, for example, that the line Au 2428 has an excitation potential of 5.0 volts, whereas Au 4241 and Au 3650 each have an excitation potential of about 8.0 volts. It is also seen that Au 2428 is an example of a ground state line.

The terms *resonance line* and *resonance potential* sometimes appear in the literature. A resonance line of an element is the line of lowest excitation potential and resonance potential is the value of its excitation potential.

2–8. Obtaining term symbols and excitation data from the literature. A knowledge of the excitation potential of a line is of considerable value in an analysis because its response (increase or decrease of intensity of emission) to a change of energy conditions in the source depends on the excitation potential of the line.

It has been shown (Section 2–7) that it is possible to obtain excitation potentials directly from energy level diagrams, as for example from those given by Grotrian (1928). Only a few such diagrams have been drawn, however, and it is customary to refer to books which list all classified line spectra.

Books of wavelength tables usually give wavelengths only, although the *M. I. T. Wavelength Tables* (Harrison, 1939) do include a few excitation potentials of the most sensitive lines. Until recently, it has been necessary to convert wavelengths to wave numbers, and then refer to Bacher and Goudsmit's book (1932), which contains all lines classified up to 1930, given as wave numbers. (The use of this book is referred to again later.) Recently, Moore (1945) has published term tables on most classified lines, given as wavelengths. In this useful publication, the lines of each element are arranged in multiplets; term symbols and corresponding excitation data are given. If in these tables the energy of the low level is given as 0, the emission of the particular line will involve the ground state of the atom. The energy of the high level is the measure of the excitation potential of the line.

The analyst might endeavor to obtain the excitation potential of a line directly from its wavelength, via the conversion factor of 1 volt = 8067 cm^{-1}.* Such direct conversion of wavelength to volts is permissible provided the low level of the line is the ground state. Otherwise the value of the low level above ground must be added to the value obtained from converting wavelength to volts. To ascertain whether or not a given line ends in the ground state entails some reference work. As a result, it is easier to consult Moore's multiplet tables in the first place, because this

*This conversion is facilitated by using the relationship, excit. pot. $= \frac{12{,}380}{\lambda}$ volts.

operation takes no more time and all the necessary potential data are given there.

Lines of wavelength less than about 2900A are not listed in Moore's tables. These tables have been prepared for astrophysical use, and since the ozone in the earth's atmosphere absorbs radiations of less than 2900A, lines of short wavelength are of no astrophysical value and have been omitted. For these lines Bacher and Goudsmit's tables may be used. Whereas wavelengths are normally given for air, the wave numbers given in Bacher and Goudsmit's tables refer to the passage of radiation through a vacuum, and in converting λ to ν' a correction must therefore be made for the refractive index of air,

$$\nu' = \frac{1}{\lambda_{\text{air}}\, n_{\text{air}}},$$

where n = the refractive index of air = 1.00029. Kayser (1925) has published tables which facilitate the conversion of λ^{air} to ν', and vice versa.

Meggers (1946) has compiled a bibliography of all papers which give line classifications, to which reference can be made in seeking term symbols and excitation data on lines. The National Bureau of Standards (Washington) is releasing a series of publications on line classification which makes available in book form all published information. The first volume has now been released (Moore, 1949) and covers these elements: H (also deuterium and tritium), He, Li, Be, B, C, N, O, F, Ne, Na, Mg, Al, Si, P, S, Cl, A, K, Ca, Sc, Ti, and V. Lines are listed in wave numbers.

2–9. Collisions of the second kind: The metastable state. Collisions of the type referred to in the preceding sections, in which an atom is excited, are known as *collisions of the first kind*. Once an atom is excited by such a collision, it may lose its acquired energy before emitting spectral lines by undergoing a *collision of the second kind*. This is a collision with an unexcited atom which either gains kinetic energy or itself becomes excited as a consequence of the collision.

An excited atom usually has a lifetime of about 10^{-8} sec, but due to the selection rules which forbid some transitions (Section 2–6), atoms in certain states are unable to return to the ground state by normal line emission and their lifetimes are much prolonged ($\gg 10^{-8}$ sec). This condition is called a *metastable state*. In the energy level diagram of the Au atom (Fig. 2–1), the levels labeled (a) and (b) are metastable. Because of the prolonged lifetimes of atoms in metastable states, collisions of the second kind become much more probable. As a result, the metastable state is of particular importance for energy transfers of this kind.

If the upper level of the excited atom of one element is similar in energy

to a possible level in unexcited atoms of another element, an energy transfer due to a collision of the second kind is much more probable. The atoms of two such elements are in close resonance and the energy transfer is usually referred to as a *resonance transfer.*

Because the transition probabilities (Section 3–5) of the intense sensitive lines are very high, and consequently the lifetimes of their upper levels very short, these lines are little affected by collisions of the second kind and their upper levels will probably play a negligible role in energy transfers.

Molecular emitters are also capable of being activated and deactivated by collisions of the second kind.

The possible importance of collisions of the second kind in quantitative spectrochemical analysis is discussed in Section 8–4.

2–10. Ionization potentials. In Fig. 2–1, the different series may be seen to converge on a limit which, as read on the volt scale, is 9.2 volts. At this potential, an atom of gold is ionized and its valency electron is removed completely from the influence of the gold nucleus. The ionization potential of an element is also obtained by setting $n = \infty$ in Eq. (2–6). An ion may also be energized sufficiently to emit a spectrum but because the ion and neutral atom have different electronic configurations, the spectrum of an ion differs from that of the atom. In the d.c. arc, most lines emitted are from the neutral atom but a considerable degree of ionization (Section 3–3), particularly of elements of low ionization potential, takes place, and ion lines are also in evidence. Lines emitted by the neutral atom are quite commonly referred to as *arc lines* and those from the ion as *spark lines.* It is less ambiguous to call them *atom lines* and *ion lines* respectively.

The spectrum of a singly ionized element resembles the spectrum emitted by the element of preceding atomic number; likewise the spectra of doubly or trebly ionized elements resemble the spectra of elements of two and of three units of atomic number less, respectively. Thus the spectra of Na, Mg^{+}, Al^{++}, Si^{+++} are similar because their electronic structures are similar; these are said to be *isoelectronic.*

The ionization potential of an element in the arc discharge is a very important parameter in determining the conditions of excitation within the arc, and is discussed in Chapter 3. The ionization potential of an element is also a rough measure of the ease with which an element may be excited; elements which have high ionization potentials are difficult to excite, whereas those of low ionization potential are easily excited.

2–11. Hyperfine structure of spectral lines. Each spectral line has a characteristic *hyperfine structure* and if a very high resolution and a great dispersion are employed, as in interferometers and in high orders of large

grating spectrographs, it is often possible to resolve apparently single lines into several components. It has been possible to interpret this small energy level splitting by introducing the concept of spin to the *nucleus* and allotting it a spin quantum number. The presence of more than one isotope is also a cause for this line splitting. Because hyperfine splitting is rarely greater than 0.1A, and is thus rarely observable under normal analytical working conditions, and because the spectrochemist is hardly likely to be called upon to undertake an isotope analysis, no more need be said about hyperfine structure.

2–12. Relative intensities of lines in a multiplet. The relative intensities of lines in a given multiplet are quite frequently given by the *sum rule*, according to which the sum of the intensities of all lines of a multiplet which belong to the same initial, or final, state is proportional to $2J + 1$ of the state not common to each line. Consider the two sodium lines already referred to; calculation of relative intensities may be made as in Table 2–2.

TABLE 2–2

Line	*Term symbols*	$2J + 1$ *of final state*	*Ratio of intensities*
Na 5889	$3\ ^2S_{1/2} - 3\ ^2P_{3/2}$	4	2/1
Na 5895	$3\ ^2S_{1/2} - 3\ ^2P_{1/2}$	2	

In this doublet, the $3\ ^2S_{1/2} - 3\ ^2P_{3/2}$ component has double the intensity of the $3\ ^2S_{1/2} - 3\ ^2P_{1/2}$ component.

Whereas the sum rule may usually be applied to simple multiplets, it frequently fails to hold rigorously for more complex multiplets. Even for simple doublets, however, some caution must be exercised in the use of theoretical intensity ratios. Thus Sambursky (1928), who examined the relative intensities of lines of the principal series of the alkali metals, found that whereas most doublets of the alkali metals of low atomic weight obeyed the sum rule precisely (intensity ratio = 2.0), several doublets of cesium and, to a lesser extent, rubidium, violated the rule, and ratios were greater than 2.0. See also Jakob (1928).

An exact knowledge of the intensity ratios of multiplet components is frequently valuable for analytical work. For example, the onset of self-absorption, which is so disastrous to accurate quantitative analysis, can be ascertained by an examination of multiplet intensity ratios (Section 7–9). Multiplet intensity ratios can be usefully applied to plate calibration (Section 9–5). Information on multiplets in a spectrum and multiplet assignment of lines may be sought in the tables of Moore (1945).

For detailed reading on spectroscopic theory and atomic structure, the reader is referred to White (1934), Candler (1937), Herzberg (1944), and Richtmyer and Kennard (1947).

CHAPTER 3

SOME PHYSICAL FEATURES OF THE D.C. ARC DISCHARGE

3–1. Excitation in the arc. When a substance is introduced into the arc by placing it in a cavity in the lower electrode (which may either be anode or cathode) the high temperature of the source causes elements to volatilize into the arc column. The rate of diffusion of material upward (away from the lower electrode) will depend on the source temperature, field force (for ions), and the mass of the atom; the rate of diffusion is approximately one meter per second.

At the elevated temperatures (3000–8000°A) at which arcs operate, several types of missiles capable of producing excitation and also ionization — atoms, ions, molecules and electrons — are present in the arc column. Impact of these missiles with atoms of a given element will cause its excitation and in the arc excitation is considered to be essentially thermal. In other words, the energy available for excitation in the arc will be largely dependent upon the temperature of the gas in the arc column. See Ornstein and Brinkman (1934) and Witte (1934). In the arc, electrons are considered to exist as an electron "gas," separate from the arc gas and with a characteristic temperature of its own. Mannkopff (1933) has shown that the temperature of the electrons is a little higher than the arc gas temperature but for practical purposes it can be assumed that all components of the arc are at the same temperature.

Although excitation in the arc is mainly thermal, and for most practical and theoretical purposes is regarded as such, the arc is not a true thermal source because of the presence of an electric field which accelerates charged particles. Examples of true thermal sources are the flame and the furnace, both of which have been used as excitation sources.

Although electrons are the lightest particles (mass of electron = 1/1840 mass of hydrogen atom), some excitation is believed to be caused by *thermal* electron impact, because electrons will move more rapidly than other particles at any given temperature, in accordance with the equation

$$\text{velocity} \propto \frac{1}{\sqrt{\text{mass of particle}}}.$$

According to Ornstein and Brinkman (1934), however, excitation of an element in the d.c. arc column is due mainly to collisions with other atoms and with molecules, and to a much smaller extent to collisions with electrons and ions. Very near the poles, electron excitation becomes more

important. Ion impact on the cathode heats it strongly and thereby causes thermionic emission of electrons. In the cooler fringes of the arc, electron and ion excitation is probably negligible, and within this region excitation is more nearly purely thermal.

In addition to the *thermal* motion of electrons they are further accelerated because of a potential difference in the arc. This difference is relatively small (see below) and electrons acquire sufficient energy only for low level excitation in the arc. A spark, on the other hand, because of a very large potential difference, is capable of high level excitation.

The arc is more nearly a source in true thermal equilibrium when the field strength is relatively small ($\sim$ 4 volts/mm) because excitation by electrically accelerated electron impact is then low. In spectrochemical analysis a gap length of about 5 mm is commonly used and as the voltage drop across the terminals is usually about 30–80 volts, the corresponding field strength is about 6–16 volts/mm. This indicates a slight degree of electron excitation. Actually most of the voltage drop in the arc occurs within the electronic free path near the active cathode spot (Meggers, 1941a). As a result, electron excitation is relatively high there and is probably extremely slight in the arc column. Field strength may be lowered by introducing into the arc column an element of relatively low ionization potential (an alkali metal).

Consider the carbon arc in air alone, that is, when no material has been added to the electrodes for analysis. The following particles will be present in the arc column:

Atoms:	N, O, C
Charged particles:	electrons, some ions* and ionized molecules
Molecules:	CN, NO, and also N_2, O_2, and C_2

Under given conditions of operation, the composition of the gas in the arc column is of paramount importance for determining the energy of excitation of the source, because temperature will depend on the effective ionization potential ($V_{i\ \mathrm{eff}}$) of this gas. The element or molecule of lowest ionization potential is particularly important in this respect (see following subheadings). For some time it had been considered that the excitation level of the arc in air was dependent on the ionization potential of nitrogen, which is 14.5 volts. Semenova (1946) points out, however, that because some carbon vapor volatilizes into the arc column, consideration must be given to the ionization potential of carbon (11.3 volts), which is considerably lower than that of nitrogen. The presence of NO, the ionization potential of which is $\sim$ 9.5 volts, somewhat less than that for carbon, and which can

* The ion concentration in the carbon arc in the air is low but is increased when elements of relatively low ionization potential are introduced.

comprise a few per cent of the composition of the arc gas, may also be important. See Mannkopff (1942) and discussion by Höcker (1946). One may consider, therefore, that the effective ionization potential ($V_{i\,\text{eff}}$) of the carbon arc in air is approximately 10.0–11.0 volts. If the resonance potential of a line of an element (Section 2–7) is less than that of the effective ionization potential of the arc, the line will be excited appreciably, whereas those elements having lines of resonance potential greater than the ionization potential of the arc in air will be excited slightly or not at all. It is a fortunate circumstance that the excitation potentials of many of the arc lines of some seventy elements (Chapter 1) lie between about 1.6–10.5 volts; consequently, the arc possesses sufficient energy to excite these lines.

Ease of excitation varies with electronic configuration. Those elements with one electron outside closed shells (the alkali metals for example) are excited most easily; those with many are the most difficult to excite (halogens and noble gases). Consequently, in moving horizontally (left to right) in the Periodic Table (see Appendix) difficulty of excitation increases. Another factor which influences ease of excitation is atomic size. Of elements which have the same number of outer electrons, those which are larger are more easily excited because the nuclear electrostatic attraction on their outer electrons is relatively weak. As a result the heaviest elements in a vertical series are usually most easily excited; compare the resonance potentials of Li (1.84 volts) with Cs (1.38 volts) and Be (6.4 volts) with Ba (1.6 volts).

3–2. Arc temperature and ionization potential. One of the earliest relatively accurate measurements of the temperature of the carbon arc in air was made by Ornstein (1931) and Ornstein and Brinkman (1931). Use was made of the intensity ratio variation of rotational components of CN bands, and a temperature of 6000–7000° A was obtained for the arc column. Lochte-Holtgreven and Maecker (1937) likewise employed CN bands for the measurement of arc temperature and obtained temperatures of 6900–7800° A for various regions of the carbon arc in air. Many other measurements of arc temperature have been made, each of which agrees in magnitude with the temperatures already given. Smit (1946) provides an extensive bibliography on relevant papers; see also Mannkopff (1942) and Höcker (1946). For a discussion of spectroscopic methods for the measurement of arc temperature see Section 3–6.

When an analysis is made, the presence of the sample elements in the arc column will change the effective ionization potential of the arc gas; hence its energy of excitation (temperature) changes. Because the sample elements will very probably have ionization potentials of less than about

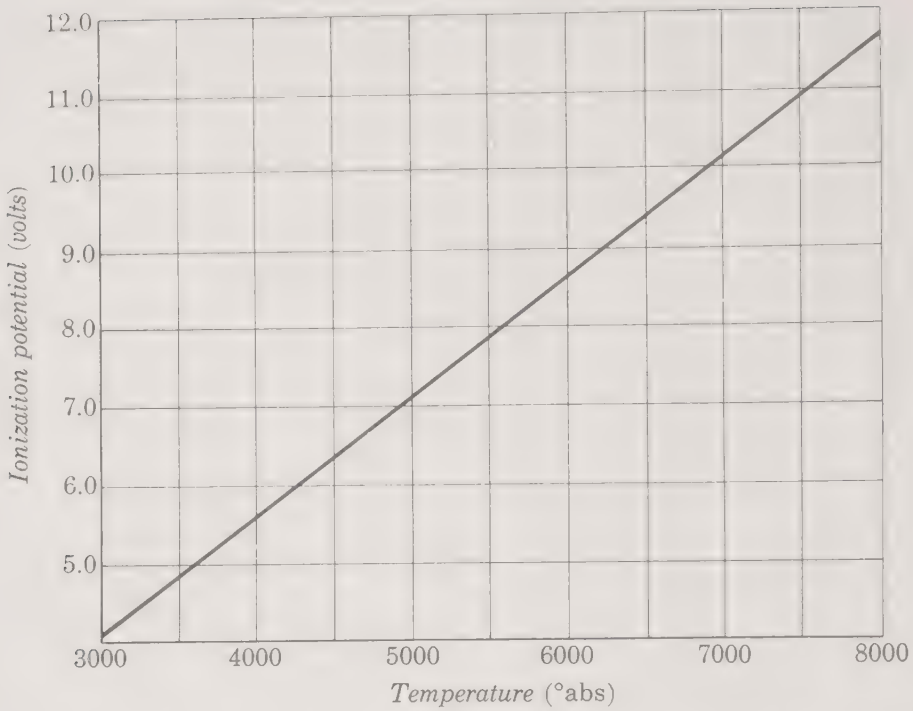

Fig. 3-1. This diagram shows arc temperature to increase regularly with the ionization potential of the constituent gas of the arc column. A maximum temperature is attained in a carbon arc in air (no material added).

Table 3-1

Arc temperatures for elements of different ionization potential, as determined from Fig. 3-1. Arranged in ascending order.

Element	Ionization potential (Volts)	Temperature (°A)	Element	Ionization potential (Volts)	Temperature (°A)
Cs	3.9	2900	Ag	7.6	5400
K	4.3	3200	Mg	7.7	5400
Na	5.1	3700	Cu	7.7	5400
Li	5.4	3800	Fe	7.9	5500
La	5.6	4000	Co	7.9	5500
Al	6.0	4300	W	8.0	5600
Ca	6.1	4300	Si	8.2	5700
Y	~ 6.6	4700	B	8.3	5900
Ce	~ 6.6	4700	Sb	8.6	6000
Ti	6.8	4800	Pt	9.0	6200
Cr	6.8	4800	Au	9.2	6400
Zr	7.0	4900	Be	9.3	6400
Sn	7.3	5200	Zn	9.4	6500
Pb	7.4	5200	Hg	10.4	6900
Mn	7.4	5200	As	10.5	7200
Mo	7.4	5200	P	11.0	7500
			C	11.3	7700

10–11 volts, arc temperature will decrease. Semenova (1946) has been able to demonstrate the relation between arc temperature and ionization potential. He used a carbon arc the current of which was kept constant at 7 amp, and used an arc gap of 4 mm. Compounds of different elements were introduced and the arc temperatures were determined spectroscopically (Section 3–6). His operating conditions were very similar to those normally employed by spectrochemists and hence his results are of considerable significance. He found that $V_i = KT$ (where V_i = ionization potential of element, T = absolute temperature, and K is a constant). The relationship between ionization potential and absolute temperature is shown in Fig. 3–1, which is adapted from Semenova. Here the range of temperatures is from about 3000–8000°A.

Using the curve in Fig. 3–1, some temperature data are given in Table 3–1. In rock and mineral analyses, matrix compositions vary enormously and the arc temperatures given in Table 3–1 will provide some indication of how source temperature changes with the composition of the material being analyzed. Most of the elements given are those which may be found as major constituents of a mineral. These values are not to be taken rigorously but serve to indicate the magnitude of the change in arc temperature with a change in composition.

Semenova also observed a linear relationship between voltage across the terminals and arc temperature, voltage $= K \times T$, where K is a constant. A current change also influences arc temperature. The effect is relatively slight, however, and a current increase from 1 amp to 13 amp increases temperature only by about 700° (Mason, 1948).

In a mineral, rock, or soil analysis, several elements normally will be present in the arc gas, and the effective ionization potential of this gas will depend on the ionization potential of each constituent element. *The element of lowest ionization potential, however, plays by far the most important role.* If the ionization potential is very low, as are those of the alkali metals for example, the effective ionization potential of the arc gas is essentially that of the alkali metal, unless it is present as a trace. Even very small quantities of alkali metal will exert a powerful influence on the arc temperature and it seems that at concentrations of about 5%* or more of alkali metal,

$$V_{i\,\text{eff}} = V_i \text{ alkali metal.}$$

Along a considerable length of the arc column there is only a relatively

* This value is very approximate and depends to a considerable extent on the method of excitation. Because volatilization is much more rapid from the anode than from the cathode (Section 5–6), low concentrations of an alkali metal in a specimen probably exert more influence on arc temperature when anode excitation is employed.

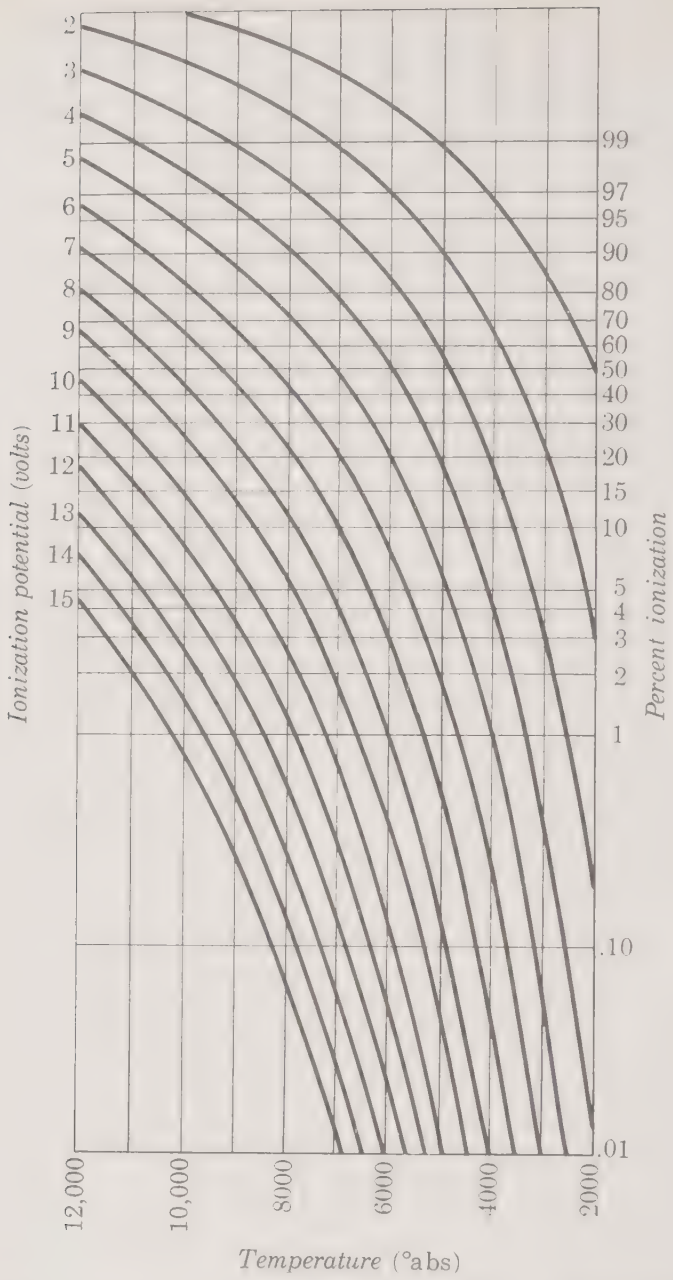

Fig. 3-2. Saha's equation at atmospheric pressure. Approximate degree of ionization of an element at any temperature may be read off this graph.

Table 3-2

Temperature (°A)	% Ionized		
	K	Ca	Zn
8000	85%	46%	4%
6000	40%	8%	0.5%
4000	3%	0.5%	0.01%

small temperature gradient, but in the immediate vicinity of the poles, temperature increases sharply. The temperature of the anode tip is somewhat greater than that of the cathode tip. Because of the prevailing high temperatures near the pole tips, elements are ionized to a greater extent in this vicinity, which in part accounts for the increase in intensity of ion lines at the electrodes — the so-called pole effects (see for example Plate 2, Ca ion lines, and also Fig. 3–6). Ionic migration toward the cathode (Section 3–4) is also a cause of line intensity enhancement (atom and ion lines) near the cathode.

3–3. Degree of ionization and temperature. As temperature in the arc is increased, the degree of ionization of any element present also increases. The relationship is given by Saha's equation, which at atmospheric pressure is

$$\log \frac{\kappa_2}{1 - \kappa_2} = \frac{-5050\ V_i}{T} + 2.5 \log T - 6.5, \qquad (3\text{–}1)$$

where T is absolute temperature, V_i ionization potential, and κ the fraction of atoms ionized.

Some data on the change of degree of ionization with change of temperature for potassium, calcium, and zinc, as calculated from Saha's equation, are given in Table 3–2. The ionization potentials of the three elements are: potassium 4.32 volts, calcium 6.09 volts, and zinc 9.35 volts.

In an arc where several elements are normally present in the gas column, Saha's equation does not hold rigorously, but the magnitudes of the values given in Table 3–2 may be regarded as indicative of what changes in ionization occur when temperature varies.

The degree of ionization may be influenced by a very high vapor density in the arc column (see discussion in Section 3–5). For convenience in obtaining the approximate degrees of ionization for elements at different temperatures, Fig. 3–2 shows a graphical plot of Saha's relationship.

Because many elements are ionized to some extent in the arc, and because many of the upper levels in the ions are not far above the respective ground states (of the ions), the arc has sufficient energy to excite ion lines. Consequently, both atom and ion lines are emitted from the arc.

The influence of degree of ionization of an element on line intensity is discussed in Section 3–5.

3–4. Cathode layer enrichment. The carbon arc in air alone, that is, in the absence of added material, possesses the highest temperature. For this reason a relatively high degree of ionization for many elements is attainable, provided that only *trace* quantities of material are introduced into the arc. Because of the electric field within the arc, ions immediately

migrate toward the cathode. Here they form an enrichment zone of ions and also of atoms (as a result of the short lifetimes of the ions) immediately below the cathode but separated from it by a very small distance. On the basis of such ionic migration Mannkopff and Peters (1931) introduced their method of cathode layer excitation which utilizes the enhanced intensity of line emission from the enrichment zone for the analysis of minerals, rocks, soils, and related materials. If relatively large quantities of element vapor from the specimen flood the arc column, the effective ionization potential of the arc gas is lowered; consequently, temperature drops, the degree of ionization falls, and the development of the cathode layer enrichment zone may become negligible. Therefore the success of the method depends on maintaining the arc gas temperature at the highest possible level. The theory of cathode layer enrichment is given here as an aid to understanding the arc discharge; practical utilization is discussed in Section 5–6.

3–5. Relative intensities of lines and temperature. During excitation of atoms and ions, many possible energy levels are involved. Transitions may take place between several possible pairs of levels, provided the selection rules are not violated. These may be regarded as in competition, and the probability that of all possible transitions a given pair of levels is involved and the corresponding line emitted, is known as the *transition probability* of the line. It follows then that lines of high transition probability are the most intense.

Other factors also influence the intensity of a line. In a source in thermal equilibrium, the populations (numbers of atoms) of various energy levels depend on temperature. If E_n is the excitation energy of a state n above the ground state, the number (N) of atoms in the state n is proportional to

$$ge^{-E_n/KT} \tag{3–2}$$

where K is the Boltzmann constant (1.38×10^{-16} erg per degree per molecule) and g the *degeneracy* or statistical weight of the state. An explanation of the term degeneracy will not be attempted here, but its meaning may be sought in some of the texts listed at the end of Chapter 2.

It follows from this relationship that the population of any energy level is sensitive to temperature, and in a thermal source populations at various levels are usually referred to as having a Boltzmann distribution. At low temperatures, low energy lines are emitted more readily, whereas high energy level lines are emitted more readily at higher temperatures. For an increase (or decrease) of temperature, the population of various energy levels increases (or decreases) exponentially with the height of the levels above the ground state. Also, the variation of intensity with change of

temperature of a high energy line, expressed as a percentage variation, is very great; high level lines are more sensitive to temperature changes.

As the component lines of a multiplet have virtually the same excitation potentials, each line responds in a like manner to temperature changes and consequently intensity relationships are independent of temperature variations.

Another factor which we have to consider when examining line intensity is the relation of the degree of ionization to temperature, as given by Saha's relationship, Section 3–3. Whereas the Boltzmann distribution determines the population of atoms (or ions) at different energy levels, the degree of ionization will determine what proportion of the total number of atoms which enter the arc is available for atom or ion emission, respectively. An increase in temperature causes a higher degree of ionization, and consequently may deplete the number of available neutral atoms, with a resulting weakening of the intensity of the atom spectrum and a brightening of the ion spectrum.

In the d.c. arc as used in analysis the degree of ionization does not influence the intensity of the atom spectrum if the element has a high ionization potential. Consider zinc ($V_i = 9.35$ volts) and potassium ($V_i = 4.32$ volts) for example, in relation to a temperature change from 4000°A to 6000°A. According to the data in Table 3–2, the proportion of non-ionized zinc will change from 99.99% to 99.5%, which is a negligible change in the number of atoms, whereas for potassium the change is appreciable — from 97% to 60%. In a source of very high temperature, ionization of the alkali metals is almost complete and there is a consequent marked weakening of the atom spectrum.

An example of how line intensity changes with temperature in some mineral analyses is provided by measurements on a pair of calcium lines, Ca 4226 and Ca 3968. The former is a low temperature line (excitation potential, 2.92 volts) whereas the latter is an ion line (*total** excitation potential, 9.2 volts). Table 3–3 gives the intensity ratios of these two

Table 3-3

Material	Ratio $\frac{\text{I Ca 3968}}{\text{I Ca 4226}}$
Carbon	1.8
Albite	0.5
Microcline	0.3

* Total excitation potential = ionization potential + excitation level above ground state of ion.

lines, for calcium as an impurity in carbon, as a trace in *albite* (soda feldspar), and as a trace in *microcline* (potash feldspar). The soda feldspar contains a trace, 0.4%, of K_2O but it is doubtful whether this small amount of potassium will influence the arc temperature, which in this mineral will be controlled by the ionization potential of sodium. Arc current is 7 amp and electrode separation approximately 5 mm.

As the operating conditions are very similar to those used for calculating the temperature data given in Table 3–2, those data may be used to calculate the magnitudes of the temperature changes. The difference in temperature between an arc on albite and one on microcline is about 500°A, and this has caused a change of 1.7 in the intensity ratio. In the two extremes (carbon-microcline) the temperature change is about 4000°A and the ratio $\frac{I\ 3968}{I\ 4226}$ is altered by a factor of 6. In contrast to the variation of the ratio $\frac{I\ 3968}{I\ 4226}$, the ratio of Ca 3968 to that of another calcium ion line, Ca 3933, remained exactly constant. This was to be expected, not only because both of these lines are ion lines, but also because they both belong to the same multiplet.

The vapor density of the arc gas apparently plays a role too. For example, in the analysis of the ash of a specimen of blood much potassium vapor was in evidence, just as in the example of the potassium feldspar. From the blood ash, however, the rate of release of potassium and other elements into the arc column was far greater and the arc gas appeared to be extremely highly concentrated. It was not possible to measure the intensities of the calcium spectra accurately because Ca 4226 was very intense, but the ratio I Ca 3968/I Ca 4226 could be estimated roughly at 0.03 or less, compared with 0.3 in microcline. Consequently calcium must have been ionized to a very slight extent. Smit and Vendrik (1948) have studied the degree of ionization of metals in a flame and point out that at relatively high concentrations of vapor in the flame, ionization is repelled. Such lowering of the degree of ionization of elements in a very dense arc may account for the increase in intensity of Ca 4226 relative to the calcium ion lines in the blood ash when compared with microcline.

The lowest possible degree of ionization (at atmospheric pressure) is obtained in the arc by flooding it with cesium vapor. This may be done by arcing a volatile salt (halide) of cesium from a carbon *anode*.

In spectrochemical analysis changes of arc temperature will naturally affect the intensity ratios of different lines in varying amounts. These variations will range from negligible variations for lines of the same excitation potential, to as large a change as shown by the pair Ca 3968 and

Ca 4226. Rarely, however, is the ratio of a pair of lines as sensitive to temperature as the ratio of these two calcium lines, and the intensity change for this pair may be regarded as an upper extreme.

Interesting observations on the behavior of atom and ion lines of calcium and strontium have been given by Rollwagen (1939). This publication contains also a useful discussion of relevant theory.

3-6. Measurement of arc temperature. Because the d.c. arc is essentially a thermal source, a knowledge of its temperature as used in an analysis may well prove to be of great value. In particular it should aid in comprehending the behavior of line intensity due to changes of matrix composition. (See Chapter 8.)

If transition probabilities and respective statistical weights of lines are known, it is possible to measure the temperature of a source in thermal equilibrium in the chief zone of emission of the particular lines. An attempt to measure source temperature by examining the intensity variation of a single line would be impractical because of many uncontrollable factors but the intensity ratio of a suitable pair of lines of one element may be used.

The intensity ratio of two lines of an element is related to temperature by the equation,

$$\frac{I_1}{I_2} = \frac{A_1}{A_2} \cdot \frac{g_1}{g_2} \cdot \frac{\nu_1}{\nu_2} \cdot e^{-(E_2-E_1)/KT}, \tag{3-3}$$

where I = intensity, A = transition probability, g = statistical weight, ν = frequency, E = energy of upper level, K = Boltzmann constant, and T = absolute temperature. Subscripts 1 and 2 refer to lines 1 and 2 respectively.

If A, g, ν, and E are known for a given line pair, a temperature determination can be made by a measurement of the ratio I_1/I_2. A and g values are known for many lines and must be sought in the general literature. Many Dutch publications in *Physica* provide $A \cdot g$ values of several lines. (See list of references given by Smit, 1946.)

From Eq. (3-3) it is evident that the greater the difference in energy of the upper levels of two lines, the more responsive is the intensity ratio to a given temperature change. An example of the use of a line pair that is sensitive to temperature variation is Cu 5153 and Cu 5700,* which has been employed by Schuttevaer, de Bont, and van den Brock (1943). The upper levels of these two lines differ by 2.26 volts, and $A \cdot g\ 5153/A \cdot g\ 5700 = 590 \pm 24$. At 5000°A, $\frac{I\ 5153}{I\ 5700} = 2.75$ and at 4000°A = 0.70; the inten-

* In place of Cu 5700, Cu 5105 was used by Sychev (1948) with Cu 5153. Cu 5700 and Cu 5105 have the same multiplet assignment.

sity ratio change is thus very marked for relatively small temperature changes. For the purpose of making temperature measurements, it is convenient to draw and use a plot of $\frac{I_1}{I_2}$ vs $1/T$.

Ion lines, as well as atom lines, may also be used for making temperature measurements and those measurements made by Semenova (1946) and used in Fig. 3–1 were made with the two ion lines Ba 4900 and Ba 4934.

In the emission of band spectra by molecular emitters (Chapter 10), the populations of molecules at different energy levels follow a Boltzmann distribution, as for line spectra, and temperature measurements can be made by a determination of band-line intensity ratios. This holds true for vibrational and rotational changes. Those temperature measurements made by Ornstein and Brinkman (1931) and Lochte-Holtgreven and Maecker (1937) and referred to in Section 3–2 were made with the use of CN emission. Coheur and Coheur (1942) have used AlO bands. As CN emission occurs mainly in the core of the arc column, temperature measurements using CN would be restricted to this region of the arc. At temperatures below 5000–6000°A, CN emission is extremely feeble. On the other hand, AlO emission occurs at relatively low temperatures (3000–4000°A) in the cooler fringes of the arc, and consequently temperature measurements made by employing AlO bands would be restricted to these regions. Likewise, because ion line emission is essentially from the hotter core of the arc, temperature measurements made with ion lines would refer essentially to this region, whereas low-temperature arc lines (the typical flame lines) could be used for temperature measurements at the outer fringes of the arc.

3–7. Natural shape and width of a line. The natural shape of a line, that is, the shape as emitted from a source and not as modified by instrumentation, is of the form shown in Fig. 3–3.

Fig. 3–3 shows a line to have definite width but because it is meaningless to refer to the total width of a line, half-widths are employed. Half-width is the width of the line at half the peak intensity and is Δ in Fig. 3–3.

In an arc as used for analysis, two main factors control the width of a line, *Doppler broadening* and *collisional broadening*.

A Doppler half-width depends on temperature, the wavelength of the line, and the mass of the emitting atom, and is given by

$$\Delta = 0.72 \times 10^{-6} \lambda \sqrt{\frac{T}{M}}, \qquad (3\text{–}4)$$

where T is the absolute temperature of the emitting gas and M the atomic weight. Lines of given wavelength are broadened at high temperatures

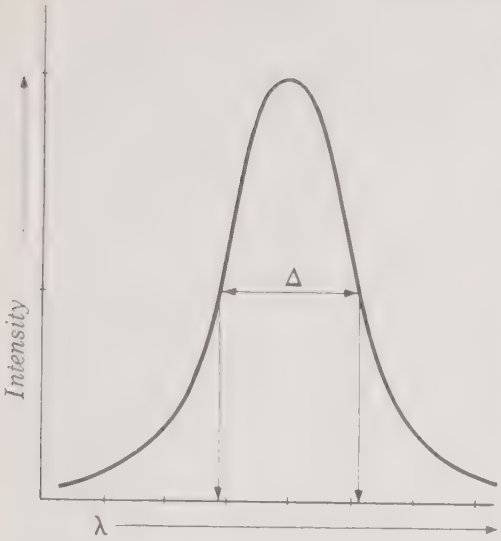

Fig. 3–3. Typical profile of a spectral line. Δ indicates the width at half the peak intensity.

and broadening increases with a decrease in atomic weight. For an element which has an atomic weight of 50, the Doppler half-width will be about 0.03A at a wavelength of 5000A and a temperature of 5000°A.

Sometimes lines are considerably broader than can be explained by Doppler broadening and this is frequently caused by collisions of emitting atoms with other atoms (*collisional broadening*). The special case of a collision between an emitting atom and an atom of the same kind is referred to as *resonance broadening*. Cowan and Dieke (1948) point out that in arcs at atmospheric pressure, resonance and collisional broadening are present to a greater extent than is usually realized. At high concentrations of an element, resonance broadening can become very considerable and may be an angstrom or more. At relatively low concentrations, the half-width of a line may be chiefly due to a Doppler effect, whereas at high concentrations, the width will be that due to resonance broadening. Resonance broadening is particularly marked for lower members of a series. The practicing spectrochemist is well aware of the presence of several broad lines; In 3256 (Plate 1) is an example.

If an excited atom is in a strong electric field, its emitted line may be broadened. This broadening is referred to as a *Stark effect* but is probably insignificant in the d.c. arc used for analysis.

3–8. Self-absorption and self-reversal. What has been said thus far about line shapes really refers only to the shape of the line at the point of emission in an arc. The emitted radiation must pass through the width of the arc, and line shape may be modified during this passage.

Surrounding the central hot core of the arc is a cooler outer fringe. Due to the prevailing low temperatures in this zone, low level excitation is possible, and this region is also the main site for the emission of some band spectra. In addition, many atoms will be present here in the ground state or very low energy states, and these low state atoms are capable of producing an absorption spectrum and hence of *self-absorption*. An absorption spectrum may be considered as the reverse of an emission spectrum. If, for example, light is allowed to pass through a column of sodium vapor

(with the sodium atoms in the ground state) and the transmitted radiation is analyzed in a spectrograph, the resultant spectrum will show two dark lines at wavelengths equal to that of the sodium *D* lines, on a bright background. A similar condition obtains in the arc. Lines of a given element radiate out through the absorbing fringe, where elements of the same kind may absorb some of this radiation, thereby causing a weakening of the emitted intensity. Because only atoms in low energy states exist in the absorbing fringe, self-absorption tends to be restricted to low energy lines. At relatively low concentrations self-absorption is usually negligible because the vapor density of absorbing atoms is low.

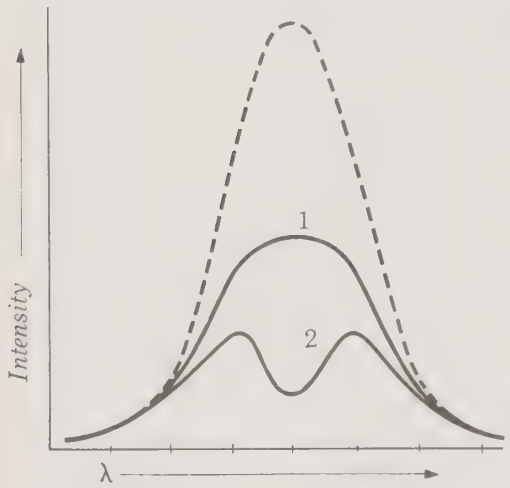

Fig. 3–4. Modification of the shape of a line by self-absorption. (1) Moderate self-absorption and (2) extreme self-absorption (self-reversal).

Because of the temperature gradient in the arc, the Doppler half-widths of the emitted lines are much greater than the Doppler half-widths of the absorption lines. Furthermore, at relatively high concentrations, there is probably much resonance collisional broadening of the emission line. Self-absorption is, therefore, greatest at the peak of the line, and a partially self-absorbed line tends to look like (1) in Fig. 3–4. The dotted line shows the profile for no absorption. The amount of self-absorption increases rapidly with concentration of absorbing vapor, as the relationship between I_0, the intensity of the emitted radiation, and I, the intensity after some absorption, is determined by an equation of the exponential type,

$$I = I_0 e^{-ad}, \tag{3–5}$$

where d is path distance and a is the absorption coefficient, which is proportional to I. See Dieke and Crosswhite (1943). Finally, in the extreme case, the intensity at the center of a line is almost wholly absorbed and the line looks like (2) in Fig. 3–4. This is *self-reversal*. Many examples of self-reversal are found in the analysis of minerals and rocks.

Plate 1 shows extreme self-reversal of In 3256 and lesser reversal of In 3258, in the arc spectrum emitted by an indium salt. The emission line of In 3256 is seen to be very broad, whereas the absorption line of In 3256

is very narrow and is restricted to the central region. See also low level iron lines in Plate 2.

From a consideration of their observations on the iron spectrum, Dieke and Crosswhite (1942) state that for given operating conditions the intensity of a line is the most important factor in determining the amount of self-absorption. Next most important is the lowness of the low level of the line.

Some observations on the significance of line intensity and lowness of low level in determining the amount of self-absorption have been made by the writer. For this purpose use was made of a "pole to pole" analysis of some lines emitted by an iron arc, the spectrum of which is rich in lines of various intensities and low energy level differences.

Along the length of the iron arc column, the thickness of the outer absorbing fringe changes rapidly and increases toward the cathode, as shown in Fig. 3–5. One would therefore expect a minimum of self-absorption near the anode and a maximum near the cathode. This is shown clearly in Plate 2, where many iron lines are shown and for several of which the respective low and high-level energies are given. Faint arc lines, for example Fe 3016.185, remain roughly uniformly intense along the arc length. These may be regarded as representing the intensity distribution for no self-absorption. Medium strong lines which do not have a very low level, for example Fe 3018.98, weaken moderately towards the cathode, whereas low-level lines of like intensity weaken much more (see Fe 3017.63). Very intense low-level lines such as Fe 2966.90 show self-reversal.

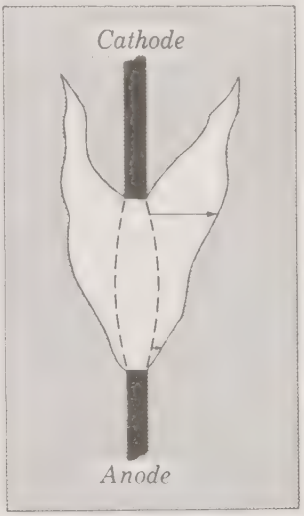

Fig. 3–5. Sketch of an iron arc. Outer flamelike fringe of the arc column is indicated by the area outside the central arc core. The thickness of this flamelike fringe increases markedly near the cathode.

Fig. 3–6 shows longitudinal intensity variations for a few selected lines in the above categories. The importance of the intensity of a line and the lowness of its low level for the degree of self-absorption should be quite evident from Fig. 3–6 and Plate 2. If two lines are of about equal intensity, a difference of 1.0 volt in the low energy levels is very significant when considering the factor of self-absorption in the choice of lines for analysis.

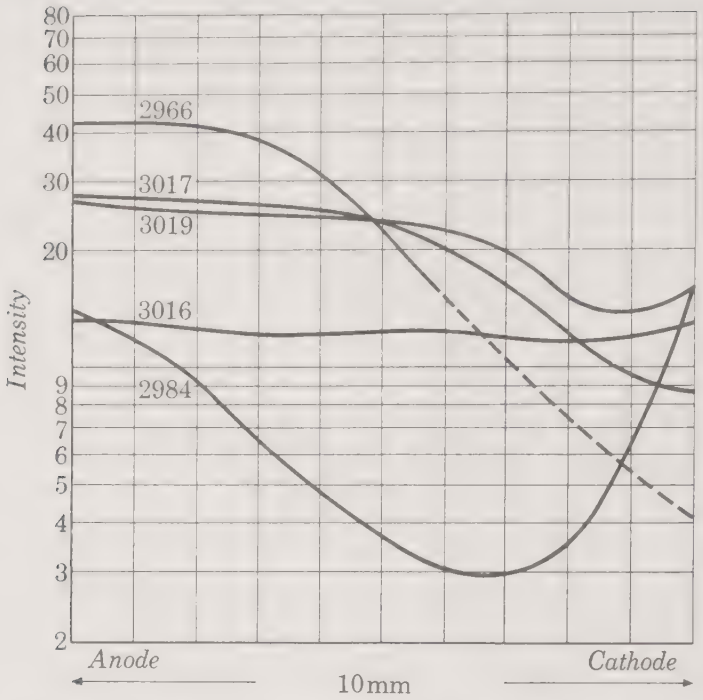

Fig. 3–6. Longitudinal intensity distribution in iron arc of several iron lines of different intensities and low energy level. The curve for Fe 3016 may be regarded as typical for an arc (atom) line showing no self-absorption. Maximum self-absorption is shown by Fe 2966, which is the most intense iron line and which ends in the ground state. Fe 2984 is an ion line and shows pole effects.

Compare Fe 3017 and 3019. If the low levels of the two lines are the same but intensity differs by a factor of 2, the difference in the amount of absorption is marked (compare Fe 3016 and 3017); consequently such a difference ($\times$ 2) is significant when considering the choice of lines for analysis.

The intensity distribution for Fe 2984 (an ion line) is also shown in Fig. 3–6. Self-absorption is probably negligible.

In quantitative analysis (Chapter 7) the onset of self-absorption frequently limits the range of concentrations that can be analyzed. Whereas it is easy to see self-reversal, the onset of self-absorption is not easily detected unless a series of standard specimens has been prepared and a working curve drawn as described in Section 9–4. In some instances it is possible to employ other methods to detect whether or not a line shows self-absorption (Section 7–9).

Whether or not a line shows self-absorption is not only important for quantitative analysis (as indicated above) but also for internal standardization (Section 7–9) and plate calibration by line intensity ratios (Section 9–3).

CHAPTER 4

POWER FOR THE ARC SOURCE

4–1. General. Because no attempt to provide particulars of instrumentation has been made in this book, circuit design and construction of arc sources will not be discussed in detail.

The d.c. arc as used in spectrochemical analysis may be regarded as an open arc in air, for which Nottingham (1926) has given this equation relating voltage and current:

$$V = A + \frac{B}{I^x}, \tag{4–1}$$

where A and B are constants, I is current, V is voltage, and x depends on the composition of the anode (for carbon $x = 1$). This equation indicates a negative potential current characteristic; as voltage increases, current decreases and vice versa.

An illustration of the current-voltage relationship is shown in Fig. 4–1 which shows plots of V and I vs. electrode separation. In this example the experimental data refer to carbon electrodes 5 mm in diameter and a line voltage of 250 volts. In analysis, the potential drop across the arc is usually between 30 and 80 volts and currents of 2–20 amp have been used; common working amperages range from 3–12 amp. In the arc column charge carriers are electrons and ions.

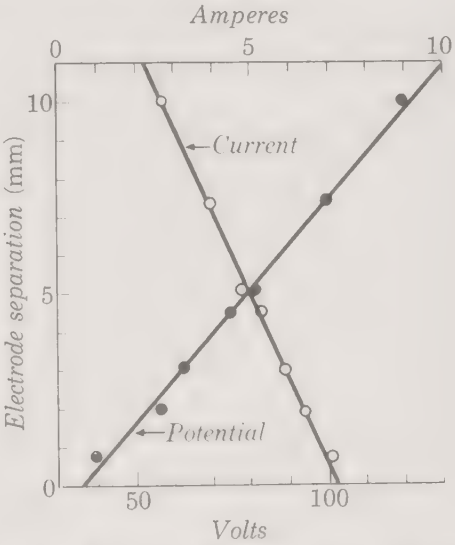

Fig. 4–1. Change of potential-current relationship with change of arc gap of carbon arc in air.

Either a motor generator or rectified a.c. (rotary converter, valve, or metal rectifier) may be employed as a source of d.c. power. Although various line voltages between 100–250 volts have been used, a relatively high voltage is preferred because of the greater steadiness and reproducibility of the arc source under such conditions. A ballast resistance is used in series and if rectified a.c. is employed a choke is required to remove wave undulations. For the analysis of such complex and varied materials as

minerals, rocks, and soils it is desirable to have available a large and easily tapped range of current, often from 2–10 amp or more. Tapping may be done by means of a tapped resistance or, if finer adjustments are required, a sliding resistance may be introduced. Additional equipment includes an ammeter and voltmeter for recording gap current and voltage respectively. The circuit design and operating details of the d.c. arc are discussed at some length by Mitchell (1948, pp. 55–59).

Levintov (1945) describes an interesting arc source in which an impulse discharge of high current density is superposed on an ordinary stationary arc discharge. Due to the arc discharge, normal volatilization of the specimen occurs, and at each impulse of the high current-density discharge there is a sudden increase in temperature. High level excitation is therefore possible, and such elements as Cl, Br, I, and S are excited by this source. Compare with elements given in Chapter 1 as excitable in stationary d.c. discharge.

4–2. Current control. Current control has often been urged as a means of attaining the highest reproducibility. The observations of Belyakov-Bodin and Mandelstam (1941) are pertinent in this respect because they suggest the degree of improvement obtainable through the use of different voltages and current control. These authors measured the intensity ratio Cu 5105/Cu 5153, using (a) a 110 volt d.c. source, (b) a 220 volt d.c. source, and (c) a specially designed rectifier for controlled current. The ouput of the latter source was nearly independent of the potential drop across the arc gap. Forty determinations were made and standard deviations were found as follows: (a) $\pm 14\%$, (b) $\pm 9\%$, (c) $\pm 7.5\%$. Cu 5105 and 5153 are both atom lines, but their excitation potentials differ enough (Δ volts = 3) to make them sensitive to fluctuations in the conditions of excitation. The significant differences in reproducibility for the three sources indicate (1) that considerable improvement may be achieved when a source of relatively high voltage (220 rather than 110 volts) is used, and (2) that some further improvement is attained in the controlled current source.

Usually it is possible to reproduce the intensity ratio of a pair of atom lines of an element more precisely than has been done for Cu 5105 and Cu 5153 and the reproducibility of the data on this pair should not be regarded as typical. The ratio of this pair was investigated because it is particularly difficult to reproduce accurately.

Some manufacturers have constructed constant-current d.c. arc sources which dispense with the use of the ballast resistance. Although these sources are of considerable value for the analysis of metals and alloys,

they supply but one amperage and are thus unsuited for the analysis of minerals, rocks, and soils, which require a wide current range.

As its name implies, a controlled current source makes available a closely controlled current. However, it does not correct for current fluctuations across the arc gap. Potter and Scott (1948) have described an automatic and electronically controlled current regulator capable of stabilizing current in the arc gap. Operating from a 250 volt d.c. supply, this regulator handles arc gap currents of 4–8 amp and maintains them within 0.02% per volt variation over an arc voltage range of 30–70 volts. An oscillographic study shows that not only has current been stabilized effectively, but voltage fluctuations have been smoothed out as well. Potter and Scott give reproducibility data in support of the claim that greater reproducibility is attainable through the use of current regulation. They further point out that whereas current control is highly desirable in the absence of an internal standard, it may lose much of its importance when internal standardization is attempted. This is due to the fact that an internal standard (Section 7–4) should compensate adequately for the intensity fluctuations of the analysis line. The choice of a good internal standard is frequently of paramount importance for the attainment of highest accuracy in quantitative analysis.

Fassel (1949) has been able to determine several of the rare earths very accurately, using another rare earth as an internal standard. The standard deviation was usually about $\pm 2.5\%$, which is excellent. Fassel makes it quite clear that the high precision he obtained was not attributable to any attempt to employ current control but to the use of a good internal standard. He points out further that other investigators who used current control but apparently did not employ the best internal standards reported standard deviations three to four times greater than his value. For most of the writer's investigations, no attempts at current control have been made and provided a good internal standard was chosen and a smooth burning arc was obtained, standard deviations of $\sim \pm 3\%$ have often been attainable. See Section 12–2, for example.

It should not be inferred here that current control is a waste of time when an internal standard is employed. Current control does improve accuracy but its importance is relatively slight when compared with the choice of the internal standard and the selection of the best operating conditions (electrode dimensions, composition of sample, arc current, etc.) to provide a really smooth-burning arc. Beginners in particular are apt to feel that the use of a current-controlled source is a panacea for the difficulties of quantitative analysis.

Fetterley and Hazel (1950) refer to a simple and cheap d.c. source unit and an auxiliary automatic current controller. By means of the current

controller current can be held constant within ±0.5 amp at any selected amperage between 5 and 15. The source unit is capable of providing an output current of up to 45 amp and is stated to cost only $100.

4–3. Multisource units. Power for the d.c. arc can also be supplied by the so-called multisource units. These provide power for several types of discharge from a single unit and through their use the properties of an arc discharge can be modified. Such units are valuable in a laboratory which handles a wide variety of specimen types, the analyses of which necessitate the use of more than one discharge type. Multisource units are, however, costly and if limited funds are available and only a d.c. power source is required it should be borne in mind that the discharge obtained from even the simplest of power units (preferably a high, 200–250 volt source) is invariably satisfactory for the d.c. arc analysis of minerals, rocks, soils, and related materials.

4–4. Intermittent (pulsating or interrupted) arcs. When using metal electrodes the d.c. arc may cause excessive melting of the electrodes, and to overcome the intense heat generated by the continuous d.c. arc, interrupted or intermittent arcs have been introduced. Landergren (1945) has described the use of such an arc for the analysis of boron in sediments, using copper electrodes (Chapter 13). It has been claimed that for some elements greater sensitivity may be attained in the interrupted arc, but there is little or no factual information to support such an assertion.

CHAPTER 5

QUALITATIVE ANALYSIS

Many of the topics discussed in this chapter — sample preparation, electrode purification, and cathode layer excitation for example — apply to quantitative analysis as well, but have been included here for the sake of convenience.

5–1. Sampling and preparation of specimen. A spectrochemist may be called upon to undertake the analysis of a great variety of materials, even if he confines himself to the analysis of minerals, rocks, and soils. The specimen submitted may be a large chunk of hard rock, for example, from which it will be necessary to obtain a small and accurately representative powder sample. On the other extreme, it might be necessary to analyze a small mineral inclusion which is discernible only under the microscope and which when isolated must be free from the presence of matrix constituents.

Sometimes the specimen has been sampled and prepared beforehand, but frequently the analyst must do this himself, and he should therefore be acquainted with the available procedures. Several are outlined here under two categories: (1) the preparation of a small representative powder from a rock or relatively large quantity of soil, and (2) the concentration and isolation of pure minerals.

A large specimen of hard rock must first be reduced to smaller fragments in a jaw-type crusher. Either the crusher used in ore-dressing laboratories, which regulates to some extent the size of fragment produced, or a simple hand press type may be employed. If necessary, smaller fragments may then be obtained by the use of a polished stainless or hardened steel block and mallet. If the original specimen is not unusually large, initial crushing may be done on the stainless steel block. The material is then transferred in small quantities to a percussion-type mortar until it is reduced to a particle size small enough to be handled in an agate mortar, where grinding and mixing are completed. After it has been crushed in the percussion mortar the specimen can be sampled down either by the usual cone and quarter procedure or by the convenient "splitter" described by Ballard, Oshry, and Schrenk (1943) and Marks and Hall (1946). This splitter can be made in several sizes so as to handle any bulk of specimen conveniently. The final grinding in the agate mortar is continued until homogeneity is ensured and the bulk of the sample is reduced to about -150 mesh; ten to fifteen minutes usually suffices.

The cleanliness of the agate mortar is discussed in Section 7–20. Mullite and wolfram carbide mortars have also been used. The latter has an extremely hard surface, but there is a possibility of some wolfram contamination. If mortar and pestle are made of the same material, they abrade each other no matter how hard they may be and hence cause some contamination. Time is saved by the use of a mechanical mortar. Further time and effort can be saved in the crushing and grinding of many silicate minerals and rocks by first heating them strongly. A quick chilling in cold water makes them much more amenable to powdering.

Some contamination, principally of iron but often of manganese and other constituents of steel (Cr and Ni for example), may be introduced during crushing and grinding. The steel block and the percussion mortar are frequent sources. As soon as the surface of the steel block exhibits pitting it should be cleaned by means of a rotating wire brush attached to a flexible, motor-driven shaft. Contamination in the percussion mortar is less than in the Plattner type. Sandell (1947) gives some data on the amount of contamination by iron when *quartz* and *feldspar* are crushed in a Plattner mortar.

Although soil-like materials are frequently fine they should not be sampled without preliminary grinding because they may contain relatively coarse fragments of *zircon*, *feldspar*, *tourmaline*, and other minerals. Because organic matter is frequently present in soils, Mitchell (1948) recommends its destruction in a furnace before arcing. This applies to all organic minerals, including coals, which after sampling are ashed prior to analysis.

Some analysts may feel inclined to sieve the specimen after it has been crushed and discard the fines, thus obtaining a sample of a mesh size which may be particularly suited for analysis. The use of such a sieved fraction could be condoned provided it were truly representative of the specimen as a whole. Different physical properties of minerals (hardness, cleavage, crystal habit) have, however, been shown to cause their preferential concentration at different mesh sizes. Johanssen and Merrit (1926) have recorded some pertinent data on *biotite*, *quartz*, *microcline*, *labradorite*, *hornblende*, and *augite*, and point out that the fines should not be discarded. Thus no attempt should be made to analyze a particular sieve fraction when a mixture of minerals is to be analyzed. The use of ordinary brass sieves may introduce Cu, Zn, Pb, and Sn in detectable quantities; Cu and Zn from the brass and Pb and Sn from solder. Sampling techniques are discussed by Ballard, Oshry, and Schrenk (1943) and Lykken, Rogers, and Everson (1945).

A variety of methods is available for the concentration and isolation of mineral grains, and the procedure chosen will depend on the type and size of mineral grain to be isolated and the composition and structure within

which it is located. Because different minerals respond differently in a magnetic field, use may be made of a magnetic separator in which the field strength may be varied. A weak magnetic field attracts *magnetite* most strongly and *hematite* and *ilmenite* to a lesser degree. Following these minerals in order of their decreasing degree of attraction are *augite*, *hornblende*, *tourmaline*, *olivine*, and *biotite*. Colorless nonmagnetic minerals such as *quartz*, *feldspar*, *muscovite*, and *nepheline* remain as a residual fraction, unaffected even by strong fields. The Franz Isodynamic Separator is a convenient instrument for making such separations.

Differences in another physical property, that of specific gravity, may also be used for purposes of separation. By preparing several liquids of varying specific gravities, "sink and float" fractions of different minerals can be obtained in separating funnels. Methylene iodide (SG 3.32), bromoform (SG 2.86), and Clerici's solution (an aqueous solution of thallous formate for dense minerals) are commonly used. These liquids can be mixed and diluted in order to obtain liquids of intermediate specific gravity. By mixing methylene iodide and bromoform or benzol, a series of liquids of graded specific gravity is obtainable by means of which granite-like rocks can be fractionated into their component minerals, *biotite* (SG 3.1), *muscovite* (SG 2.85), *quartz* (SG 2.65), *oligoclase* (SG 2.64), and *orthoclase* (SG 2.56). Some very basic rock types are made up of such heavy minerals as *ilmenite* (SG 4.84), and *garnet* (SG 4.20), *titanite* (SG 3.50) and *diopside* (SG 3.29), and these mineral fractions can be separated by means of a thallium formate-water solution. Care must be taken in these separations lest contamination occur; the use of Clerici's solution, for example, introduces thallium. The heavy minerals just mentioned do not contain thallium in quantities capable of spectrochemical detection and this element is therefore never sought in them. In the lighter minerals found in granite-like rocks — *orthoclase*, *muscovite*, and particularly *biotite* — thallium is normally detectable, but for the separation of these minerals, the thallium-free methylene iodide solution is used.

If the specimen is of very coarse texture, it is sometimes possible to isolate minerals by hand-sorting after some preliminary rough crushing. For example, books of *mica* can often be obtained from coarsely crystalline pegmatite specimens in this manner. A low-power binocular appropriately mounted is an aid in the examination of somewhat finer material, from which mineral fragments may be isolated with a pair of tweezers. McClellan (1945) describes the analysis of sulfide ores which had been hand-picked with the aid of a microscope. As a result of careful sampling he was able to show that in the mixture of sulfide ores indium was present only in the lead minerals.

For some ore types, a dentist's drill has been used to bore out a tiny

fragment of the mineral sought. Moritz (1932) describes the necessary equipment, the main units of which are a small motor-driven drill and an ore microscope. Using such a drill technique, Schneiderhöhn (1929) was able to isolate some pure minerals from rocks of the Bushveld Igneous Complex (Transvaal) for spectrochemical analysis. The analyses provided very significant data on the distribution of platinum in these rocks, and are excellent examples of the effective use of spectrochemical analyses on carefully sampled specimens. Moritz (1933) employed a similar sampling procedure in his investigation of sulfide ores from Tsumeb, South West Africa. See also Haycock (1931) and Rennhackkamp (1949).

When such a micro-sampling technique is used, a section of the ore specimen is cut, then polished. When examined microscopically in reflected light, several types of mineral grains appear in sharp relief and may be drilled out. It is often impossible to obtain more than a very small quantity (a milligram or less) of mineral when a microtechnique is used, and if a sensitive qualitative test is desired cathode layer excitation (Section 5–6) is indicated.

The flotation techniques used in ore-dressing laboratories are an effective means of obtaining pure mineral concentrates. These methods may be modified for use on a smaller scale in analytical laboratories, and small flotation cells may be purchased.

If the mineral to be analyzed is very rare it is necessary to use a large bulk of specimen. Thus, to obtain a sufficient number of grains of *cassiterite*, *titanite*, *zircon*, and *rutile* for spectrochemical analysis, Frankel (1942) used 2–5 kilograms of rock.

5–2. Further preparation of specimen prior to arcing. Although it is quite common practice to load the powdered mineral as such into the electrode cavity, the resultant burn of the arc is often unsatisfactory. Many mineral and rock types behave erratically and spatter badly unless the composition of the specimen is altered. Many sulfide minerals and fine-particle clays are examples. The former spatter excessively, and the latter tend to be wafted out of the cavity when the initial arc contact is made; fine-powdered alumina may also exhibit this latter tendency.

Loss of material at the time of initial arc contact is usually due to a sudden excessive release of gas from the specimen. Organic matter, water, and carbonates are common sources of such gases (organic gases, H_2O vapor and CO_2); these may be removed by a preliminary ignition prior to arcing. This may be done in a muffle furnace. Alternatively, the loaded electrode is inserted into the tip of a laboratory burner for a few minutes. Such an ignition may volatilize arsenic, mercury, or other highly volatile elements, however, and the possible loss of these elements must be taken

into consideration. The mineral *vermiculite* has first to be "expanded" (strongly heated) prior to arcing, otherwise this peculiar mineral rapidly expands in the electrode cavity and is immediately ejected. Interlayer water is the cause. Material loss from the electrode cavity can frequently be countered by compounding the powdered sample into a tablet or pellet. For this purpose a micropress (sometimes referred to as a briquetting press) can be constructed in accordance with instructions given by Harrison and Ralph (1943), who list several publications on the use of pellets. When compounded into a pellet, some materials burn more smoothly than when packed as a powder into the electrode cavity.

The use of a carbon lid placed over the cavity to prevent loss of material has been recommended by Borovik (1943 b) for the analysis of sulfide minerals. Some general aids in overcoming loss of material have been discussed by Ahrens (1945a). The use of a very low initial amperage is sometimes helpful because its action is not so violent and the surface of the sample may fuse and adhere to the crater wall, particularly if the electrodes are not drawn apart until a few seconds after the arc has been struck. The amperage can then be increased as desired. A little NaCl, Na_2CO_3, or SiO_2 placed above the specimen in the cavity may fuse and seal it off, thus preventing its ejection.

Minerals rich in aluminum, *mica* and *feldspar* for example, are very difficult to arc successfully to completion unless mixed with an appropriate compound. After the arc has run for some time, the alkali metals and a major portion of silicon will have distilled. The residual bead or globule is chiefly alumina, which is difficult to arc and which has the annoying tendency to hop out of the electrode cavity.

Admixture of powdered carbon or graphite with the specimen is very common practice and many operators do this as a matter of routine. The arc is usually steadier then, selective volatilization (Chapter 6) is not nearly so marked, and the formation of an alumina rich residual globule in aluminum minerals is prevented. Admixture of powdered carbon or graphite is consequently often advantageous, even though CN band emission is intensified. Generally the ratio of carbon to specimen is equal to or greater than 1:1 and a 2 (carbon): 1 (specimen) ratio is quite commonly used. Higher carbon dilutions have been used, particularly in quantitative analysis, but are not recommended for qualitative analysis, where the highest sensitivity is required.

Analysis of some volatile elements which have their most sensitive lines in the region of CN bands can be spoiled by admixture of carbon or graphite (see Section 10–2).

Although powdered carbon or graphite are the substances most commonly added to the specimen to improve its burning characteristics in

the arc, many others have been used for this purpose. Some of the commonest of these are Na_2CO_3, NaCl, Li_2CO_3, SiO_2, borax, NaF, $(NH_4)_2SO_4$, NH_4Cl, CuO, Ga_2O_3, Ag_2O, $K_2S_2O_7$ and Ge metal. Of these, the ammonium salts behave in some respects in the same way as powdered carbon and have been used in preference to carbon by some operators. On arcing, the quick release of ammonia gas wafts the specimen readily into the arc column. Hasler (1941) has described a technique in which NH_4Cl and a specially designed electrode are used. The specimen is very readily volatilized into the arc column and the total exposure time is only about four seconds; this type of arc has been termed a "high streaming velocity arc." Churchill (1945) has described various arcing techniques, including the use of admixed NH_4Cl and carbon. He points out the advantages of carbon over the ammonium salts; not only does admixed carbon provide a greater sensitivity, particularly for elements like Zr, Mo, and Nb, but the arc burn of many substances shows greater improvement.

Many of the compounds listed above, in particular the salts of the alkali metals, act as spectroscopic buffers (Section 8–3). Several operate as fluxes. A flux is often important in analysis because of its power to break down mineral structures and thus remove the possibility that line intensity will be influenced by a difference in crystal structure (Section 8–7).

Sulfide minerals readily respond to attack by mineral acids and some analysts treat the powdered mineral with HNO_3, thereafter taking the solution to dryness, and arc the residual powder. Silicates are easily attacked by hydrofluoric acid, and the use of dried fluorides for this purpose is discussed in Section 6–3.

Once properly sampled and ground, the specimen is ready for analysis; it is then loaded firmly, after admixture with other materials if necessary, into the cavity of the electrode. The lower electrode is often made the anode (*anode excitation*), but may instead be used as the cathode (*cathode excitation*). A particular method of cathode excitation, namely *cathode layer excitation*, is discussed in Section 5–6. The powdered specimen is loaded into the electrode cavity (recess) with the aid of a small flat spatula. To ensure firm packing of the specimen, a stainless steel pin of a diameter slightly smaller than that of the cavity may be used to press the material home. For small-diameter electrodes such as those typically employed in cathode layer excitation, loading may be facilitated by the use of a small paper collar as described by Mitchell (1948).

Once the lower electrode is loaded and both electrodes are in position, the arc is started by one of three methods. First, a contact can be made by lowering the pointed upper electrode until it touches the wall of the lower electrode or the sample itself if it contains carbon or graphite admixture. If no carbon has been added the arc will not usually start if contact

has been made to the sample alone. Second, contact can be made by drawing a carbon rod deftly across the gap. A third method involves the use of an auxiliary circuit which momentarily induces a high-frequency, high-voltage and low-current spark across the gap, thereby triggering the arc discharge (Brockman and Hochgesang, 1942).

5–3. Electrode impurities and electrode purification. The two forms of the element carbon, "carbon" and graphite, are the materials most commonly used for electrodes in spectrochemical analysis. Other materials, silver and copper for example, both of which are obtainable in a very high state of purity, have on occasion been used. The high cost of silver precludes its general use for electrodes.

Copper electrodes are not popular because the spectral sensitivity of most elements is in general lower than when carbon or graphite is used. Furthermore, they are not easily fashioned and cannot be used if copper is sought in the specimen. The poorer spectral sensitivity is due in part to the fact that the ionization potential of copper is lower than that of carbon and as a result the copper arc is cooler and less conducive to high-level excitation. Also, the rate of volatilization from a copper electrode may be prolonged excessively. The use of copper has, however, two distinct advantages. First, copper is obtainable in a very high state of purity, particularly with regard to boron, an omnipresent impurity in carbon and graphite which is often difficult to remove. Second, because CN emission is absent from a copper arc, those lines which suffer interference from CN bands can be used.

Naturally, the use of carbon and graphite electrodes is feasible only when they may be obtained in a high state of purity and at a reasonable cost. Common impurities in carbon and graphite are Ca, Mg, Sr, Ti, Fe, Cu, B, V, Mn, and Si. Others have sometimes been reported. Usually carbon and graphite are obtainable in two forms, a relatively cheap impure grade likely to exhibit the presence of most of the impurities listed, and a much more expensive high-grade type which should show slight traces of only such elements as boron, silicon, and perhaps a few others.

Fortunately, most of the impurities detectable in carbon or graphite are the major constituents of minerals, rocks, and soils. Hence they are rarely sought qualitatively. Even when they are sought, the quantities to be estimated are often so high that electrode impurities can be regarded as negligible. As a result, the so-called high-grade electrodes may frequently be used without purification. The low-grade carbon is generally unsuited for qualitative analysis but may be used for the quantitative analysis of those elements not present as contaminants.

The need for electrode purification in any given instance depends, of

course, on the type and quantity of element to be sought and, to a lesser extent, on the arcing technique employed. Generally speaking, cathode layer excitation (Section 5–6) demands a higher state of electrode purity because of the inherent tendency of this method to reveal electrode impurities. Interference has been reported, for example, in the cathode layer excitation analysis of copper (Wager and Mitchell, 1943) in rocks. The author's personal experience with anode excitation has shown that whereas occasional interference from electrode copper was detectable in a high-amperage arc, a low-amperage arc was satisfactory even for the analysis of specimens which contained the merest traces of copper, as in granite for example.

When in doubt, some operators may feel inclined to make a blank examination by arcing the electrodes only under normal operating conditions. Whereas such an analysis may give some indication of purity, it is not a true test because the presence of a specimen in the electrode cavity has often been observed to enhance the intensity of the impurity lines. Webb (1937) and Webb and Fearon (1937) have reported the enhancement of impurity lines of Ti, V, and Li in graphite when it is arced in the presence of alkali metal compounds. This has also been the experience of Borovik and Borovik-Romanova (1937), who observed lines of Ti and V in electrodes only after the addition of KCl, NaCl, K_2CO_3, or SiO_2; the addition of Pb_3O_4 had apparently little or no effect.

If a few drops of HCl are allowed to seep into an electrode and it is then dried and arced, enhancement of impurity lines may frequently be observed. Probably the presence of material in an electrode cavity tends to increase the intensity of impurity spectra for one or more of the following reasons. (1) The arc in pure carbon is so intensely hot that elements such as lithium may become strongly ionized and emit their arc spectra poorly, whereas the presence of foreign material frequently cools the arc and produces conditions more conducive to emission of some lines. (2) Some impurity fluxing is often possible. Here the electrode surface is wetted by the molten globule, some reaction takes place, and the surface impurities are converted into more volatile forms. (3) An enhancement of intensity may appear only as a result of the presence of a much-weakened background when some material is present in the electrode.

Two general methods are used in electrode purification. The first utilizes a high temperature to release impurities, whereas the second is a method of liquid extraction. Some analysts, for example Standen and Kovach (1935) and Zurrer and Treadwell (1935), have pre-arced the unloaded electrode so as to burn off impurities. By this procedure surface impurities are usually released, but there appears to be some doubt as to whether more deep-seated impurities are adequately removed (Smith, 1946). More

commonly, one of two other heating methods is employed; either the electrodes are heated in a furnace or by passage of a very high current through them. Heyne (1930, 1932) was one of the earliest operators to employ a high-temperature purification. He found that the purity of the product could be improved by heating the electrode in the presence of chlorine or a mixture of nitrogen and carbon tetrachloride. His results (Table 5–1) give some idea of the degree of purification attained.

Table 5-1

Element	No treatment	2800 - 3000°C in N_2 + H_2	2000°C in Cl_2	2000°C in N_2 + CCl_4
Fe	++	-	-	-
Mn	++	-	-	-
Cu	++	+	-	- to +
Si	++	+	-	-
Mg	++	+	-	-
Ca	++	++	-	-
Ba	+	-	-	-
Al	++	-	-	-
B	++	+	+	- to +
Ti	+	+	-	-
V	++	+	-	-

The +'s are a rough measure of line intensity. The efficacy of such treatment is very evident in the presence of chlorine.

Rusanov (1934) points out that even below a temperature of 2480° C., Fe, Si, Al, Ti, and V are in part released from carbon, and many elements are quickly and almost completely released at a higher temperature.

Of the two general heating techniques, the use of a high current passed through the electrode appears to be the more convenient. Currents of at least 150–200 amp are necessary and a current as high as 650 amp has been used, but at this high current there is considerable danger of a violent explosion of the carbon rod (Deinum, 1946). Gatterer (1941) remarks that a current density of 15 amp per sq mm is adequate for rods of 5 mm diameter. The duration of heating is usually about 15–60 sec.

Electrodes thus purified invariably contain B as an impurity, as well as extremely slight traces of Si, Ca, Ti, and perhaps a few other elements. Much depends on the nature and impurity content of the carbon prior to heating. The presence of slight traces of silicon and a very few other elements is in general of no consequence for the analysis of minerals and rocks, but the presence of boron can be a source of difficulty. For this

reason, some analysts have employed copper electrodes for the analysis of boron in rocks and soils because their boron content is very low, and electrode boron might therefore interfere (Chapter 13).

Methods of liquid extraction have also been employed quite frequently, but in general they appear to be more tedious without offering a purity of product greater than that obtainable by the use of intense heat. Standen and Kovach (1935) boiled carbon rods in aqua regia and after treatment with concentrated ammonia heated them in an atmosphere of ammonia and chlorine at 1000–1100° C. Staud and Ruehle (1938) have found H_2SO_4 more effective than aqua regia, HNO_3, or HCl. They describe a method in which the electrode rods are cut to shape and after preliminary heating to redness in a silica dish are cooled and refluxed with 1:1 H_2SO_4 for 24 hours. Refluxing is followed by a wash by decantation and by boiling in distilled water. After a final wash, the electrodes are again heated to a bright redness. Table 5–2 indicates the efficacy of this treatment.

Table 5-2

Original impurities	Impurities after treatment
Al	none
B	unchanged
Ca	trace
Cu	faint to none
Fe	faint to none
Mg	trace
Mn	none
Si	unchanged
Ag	none
Na	trace
Ti	none
V	none

As with heat treatments, B is unresponsive to liquid extraction and, with Si, remains unchanged. An attempt to remove Si with HF was unsuccessful.

Cholak and Story (1938) steeped electrodes for 48 hours in a 1:1 mixture of HCl and HNO_3 at 70° C. The solution was changed 4–5 times and the electrodes were then washed in four or five changes of distilled water at 70° C and finally heated in a muffle furnace at 1000° C for one hour. B, Si, Mg, and V remained as impurities.

In methods of liquid extraction, the time factor may be very important. Thus Mather (1947b) found that after a 12–15 day treatment of impure

graphite with HCl or HNO_3, a very satisfactory product of high purity was obtained. This makes it possible to employ low-grade graphite, which is far cheaper than the high-grade graphite, for almost all purposes.

A complete bibliography on electrode purification is given by Strasheim (1948), who also records several observations of his own in some detail.

The tenacity of boron in carbon and graphite may be due in part to the formation of boron carbide. This compound is extremely difficult to volatilize. So-called Acheson graphite is prepared from carborundum (SiC) which when heated at 2200°–2240° C decomposes into its component elements. Silicon volatilizes and a residue of graphite remains. Some SiC, as well as other carbides present in the carborundum, will be present as impurities. The carbides of many elements are very stable and boron carbide (B_6C?), for example, is still more stable than SiC and even at 2800° C does not decompose. If some boron nitride (BN) forms it is extremely stable (m. pt. 3000° C); the structure of this compound is the same as the graphite structure. All forms of carbon, except diamond, have the layered graphite structure. "Carbon" sublimes at about 3540° C, whereas graphite melts at about 3530° C.

Spectrochemists are not the only group disturbed by traces of boron in graphite. The presence of such traces has been a serious factor in the construction of successful nuclear reactors (piles) because of the very high slow neutron-capture cross section of boron. The purity of graphite for reactors is discussed by Doan (1946).

Both graphite and carbon are commonly used for electrodes. Because graphite is much softer and therefore more easily worked than carbon, some analysts prefer it. In addition to this difference of properties, there is another which requires consideration when a choice is made. Graphite is a much better heat conductor and as a consequence the tips of graphite electrodes are much cooler than those of carbon. This results in a marked difference in the rates of volatilization of specimen. Observations on the anode excitation of silicates have shown that the period for complete volatilization of a sample may be shortened by a factor of two or three when a carbon anode is used in place of one of graphite. Although the electrode tips have considerably different temperatures in carbon and graphite arcs, the arc column temperatures should be about the same because in both arcs in air, temperature will be largely dependent on the ionization potential of carbon and of NO (Section 3–1). Excitation levels should therefore be the same. In general, selective volatilization is more marked when graphite electrodes are used. Irrespective of whether the lower electrode is graphite or carbon, it is generally more satisfactory to use carbon as the upper electrode because it usually decreases wandering of the arc over the upper electrode surface.

Graphite is a much better conductor of electricity than carbon.

5–4. Electrode shapes and sizes.* In analytical work the greatest differences in operating procedure often center around the various electrode types used. Whereas it is common practice to employ a pointed upper electrode, each laboratory appears to develop its own pet shapes and sizes for lower electrodes. As a result, many different varieties of electrodes have been discussed in the literature. Churchill (1945) and Ahrens and Liebenberg (1946) have made some general comparisons of the different types. Several are illustrated in Fig. 5–1. Only brief comments on the use of some of these types are given here. The operator should try various shapes and sizes in order to appreciate fully the advantages and disadvantages of each for the particular purpose at hand.

Type 1: This simplest of shapes has been suggested by Wainer and Dubois (1941), but if optimum sensitivity is desired it is not recommended. See also Austin and Bassett (1943) and Ahrens and Liebenberg (1946). One advantage of this type is that the loss of a residual globule of the relatively involatile elements is avoided. Because the powdered specimen lies flat on the electrode, several very small molten globules are formed instead of a single large one, and this condition tends to smooth out selective volatilization.

Type 2: This type favors the formation of a single globule, particularly in silicates. As a result selective volatilization can easily be studied. Sensitivity is in general poor, however, and the residual bead in which the relatively involatile elements are concentrated is often lost from the electrode. Drilling a smaller recess below the main cavity frequently prevents the loss of the bead and is therefore an aid in the detection of such elements as Zr, Sc, Y, and La in silicate minerals and rocks.

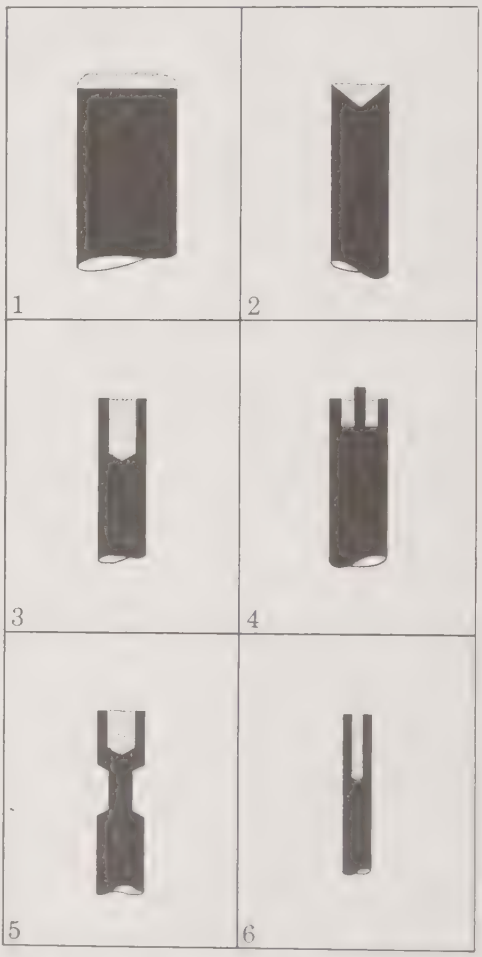

Fig. 5–1. Some typical electrode shapes. Nos. 1–5 may be used for anode or cathode excitation; No. 6 is typical of the types used for cathode-layer excitation. Drawn to scale.

*See also description of anode shapes by Harvey (1950).

Type 3: This shape provides much greater sensitivity, especially for relatively volatile elements, than either 1 or 2. As in type 2, there is a tendency to lose the residual alumina bead in silicates (unless powdered carbon, graphite, or other suitable compound is added, Section 5–2) and a small cavity drilled below the main recess has been found an aid in retaining the bead. An electrode of this shape is generally employed by the author for qualitative analysis, but not necessarily for quantitative analysis, for which (if there is sensitivity to spare) a steadier and more reproducible burn can sometimes be obtained by using a smaller diameter.

Type 4: According to some analysts, the center-post electrode produces a smoother-burning arc. Harrison and Bassett (1941) recommend its use for the analysis of the readily volatile elements in various ceramic materials. A center-post anode has been described by Hasler (1941) for analysis with his so-called high streaming velocity arc. A graphite sleeve is set into a steel electrode, which supports a coaxial central graphite rod. The powdered specimen is mixed with NH_4Cl and packed into the space between the sleeve and rod. A paper by Hasler and Dietert (1941) describes three different electrode shapes, including the center-post variety.

Type 5: A far greater heat intensity may be attained in the electrode cavity if the electrode diameter is considerably decreased below the cavity, because heat conduction is lowered. Materials otherwise difficult to volatilize can thus be arced more successfully. The characteristics of the type 5 electrode are discussed in considerable detail by Foster (1941). This type is in quite common use in several laboratories, and B. F. Scribner (1949) of the National Bureau of Standards favors the use of a modification of a type 5 electrode. See also Scribner (1948).

Type 6: Comments on electrode types have thus far been restricted to those used for anode and cathode excitation. They do not apply to cathode layer excitation because the quantities of specimen accommodated by these electrodes are excessively great for optimum development of cathode layer enrichment. Type 6 is a typical electrode employed for cathode layer excitation. The internal diameter of cathode layer electrodes is usually about 1.0 mm, and the outside diameter approximately 3.0 mm. The small diameter electrode is also used as an anode in quantitative analysis if there is sensitivity to spare, that is, if the detectability of some elements is not lost by using a small quantity of sample.

In all cavity-type electrodes various depths have been used. Here much depends on the volatilities of the elements sought. For the detection of relatively involatile elements, a shallow-depth cavity (1–3 mm) may be used, whereas for a high sensitivity of detection of the very volatile elements a deep cavity of 8–10 mm is recommended. For general work a depth of 4–6 mm is commonly employed. A specially designed electrode for the

analysis of mercury, which is the most volatile of all elements, is described in an advertisement of the National Carbon Company (1949).

A lathe may be used for the shaping of electrodes, but special electrode cutters are more commonly employed. An exhaustive bibliography on electrode cutters is given by Mitchell (1948, p. 62) and Myers (1950).

Although analysts invariably pay considerable attention to the size and shape of the electrode crater for holding the powdered specimen, the importance of the crater wall thickness may be overlooked. This has been emphasized by Strock (1948 b) and is particularly important when anode excitation is employed. A very thin wall is likely to be consumed very quickly, leaving a large bulk of material without wall support and which may therefore easily fall from the electrode. If a very thick-walled electrode is used the sample will probably be consumed more rapidly than the crater walls, particularly if the sample constituents are volatile. This is of no consequence provided the specimen volatilizes cleanly, because the arc may be stopped as soon as there is evidence that the specimen has been volatilized completely. The exposure need not be continued until the crater walls are completely consumed, and excessive CN emission is avoided. Some elements, however, tend to form a small seepage residue at the bottom of the crater. A much longer period of arcing is then necessary because although the main bulk of the specimen may have volatilized earlier, the unconsumed crater walls and the surface of the crater itself will have to be vaporized completely before the arc will release the refractory elements. CN emission is likely to be excessive in this case. Consequently the crater wall thickness should be so adjusted that specimen and wall are consumed at about the same rate. This is a general recommendation for most work.

The general technique used by the author for the qualitative examination of the most common rocks, minerals, soils, and allied materials is as follows. Two type 3 electrodes are required. In one, the powdered sample is loaded untreated and unmixed with any compound, unless the specimen contains less than a few per cent of alkali metals, in which case 5–10% of NaCl or KCl is added. (The presence of alkali metals serves to depress the cyanogen background, Section 10–2.) In the other electrode a mixture of 1 part sample and 2 parts powdered carbon is loaded. The undiluted specimen is arced for about 1–3 minutes at approximately 3 amp. The plateholder is then racked down and the second (+ carbon) electrode is arced at 7 or more amp to completion. At intervals of 30–60 seconds of this second exposure the plateholder is racked down. A slit length of 3 mm is used in each instance and a variable sector, adjusted to transmit $\frac{1}{8}$ of the total incident radiation, is rotated across half the length of the slit. Use of the sectored portion of the spectrum often facilitates the

identification of relatively weak lines in a heavy background, particularly in the cyanogen band region.

Low amperage and the presence of alkali metal are used to provide a high sensitivity for several volatile elements, notably those whose most sensitive lines fall in the cyanogen band region (Section 10–2). Admixture of powdered carbon and the use of a high amperage ensure that the sample is completely consumed and that the less volatile elements are thereby vaporized.

5–5. Less conventional methods of introducing the elements into the arc column. In lieu of vaporizing the specimen into the arc by loading in an electrode, other methods have been used for its introduction. Rusanov (1940) has described a method of introducing the specimen by placing its powder on a strip of filter paper which is then fed into the arc. See also Rusanov and Alekseeva (1941). In a method described by Toisi (1940) the powdered specimen is allowed to fall from above into the arc column for a period of about ten seconds. The electrodes are inclined toward each other and about 0.35 gm of specimen are used. When such large quantities of material are excited in the arc, a relatively low limit of detection is expected. Sergeev (1940) discusses a novel procedure in which a magnetic field is utilized to draw material into the arc.

Preuss (1940) has described a method which employs 1–3 gm of specimen, placed in an electrically heated carbon tube furnace. The furnace is gradually heated to about 2000° C and the escaping vapors are blown into a carbon arc through a second tube which serves as a cathode. According to Preuss, this procedure has a high sensitivity for the volatile elements Zn, Cd, Hg, In, Tl, Ge, Sn, Pb, and Bi. The sensitivities and lines used for each element are given in Table 5–3.

Table 5-3

Element	Line	Limit of detection %
Zn	3345	0.0001
Cd	3261	0.00001
	2288	0.000001
Hg	2536	0.00001
In	3256	0.000003
	3039	0.000003
Tl	2767	0.000003
Ge	2651	0.000003
Sb	2598	0.00003
Bi	3067	0.000003

Preuss has been able to detect and estimate these elements in silicate rocks and also in soils. The potential value of this general technique is very great because most procedures fail to detect several of these elements in rocks and soils. As a result, their geochemistry is imperfectly known. Other furnace techniques have been reported by Rose and Böse (1935), Böse (1936) and by Ottemann (1940). Table 5–4 gives some analyses by Preuss (1940) of granite, gabbro and clay. Most of the concentrations given are below the normally detectable limits.

Table 5-4

Specimen	Element					
	Cd	Hg	In	Ge	Sb	Bi
Mixture of 36 clays*	0.00003	0.00003	0.00005	0.0007	0.0003	0.0001
Mixture of 14 granites*	0.00002	0.00001	0.0002	0.0003	0.00003	0.0002
Mixture of 11 gabbros*	0.000003	0.00001	0.00003	0.0002	-	-

*All from Germany

A double-arc procedure described by Shaw, Joensuu and Ahrens (1950) is similar in principle to the auxiliary furnace techniques, but is simpler to operate. The "furnace" is an electrode placed within the usual arc area. This electrode is hollowed and accommodates about ½ gm of specimen, mixed thus: 3 parts specimen and 1 part mixture of 90% Li_2CO_3 + 10% NH_4Cl. One arc heats the bottom of the furnace electrode and another excites the distilled vapors. A detection limit of about 0.000001% has been reached for thallium.

For observations by Veselovskii (1941) on vacuum sublimation of volatile elements in *chalcopyrite* and *pyrite* see Chapters 20 and 21.

The high sensitivity of furnace techniques refers only to extremely volatile elements. De Rubies and Doetsch (1935) have developed a procedure which enhances the sensitivity of the very involatile elements. This method has been applied to the analysis of lead minerals, chiefly *pyromorphite*. Specimens of 50 mg were arced almost to completion, that is, until the bulk of the elements had been volatilized and a small residue of involatile elements was left. This operation was repeated until about 1.0 gm of specimen was consumed and an appreciable refractory residue had been built up. On arcing this residue it was possible to detect Y, La, and other rare earths. De Rubies and De Azcona (1936) further applied this general technique to concentrate a residue of involatile elements from as much as 10 gm of *sphalerite*. These authors claim for several of the involatile elements an increase in sensitivity by a factor of 200 over normal arcing procedures.

A very high sensitivity may be obtained for many elements by first concentrating them chemically (Section 7–21).

5–6. Cathode layer excitation. Whereas the use of anode excitation involves no meticulously careful attention to operating details, the same cannot be said of cathode layer excitation.

The theory underlying the enrichment of atoms near the cathode and the consequently greater intensity of emission of their lines from this region under certain conditions of arcing has been given in Section 3–4. Mannkopff and Peters (1931) were the first to describe and introduce cathode layer excitation as a method for the analysis of rocks and minerals. Following their report the method was widely applied, first at Göttingen and later elsewhere in Europe. In the United States, cathode layer excitation has not enjoyed the same popularity, although it has been employed in several instances. Plate 3(2), which was obtained by arcing about 10 mg of sample in a small cathode, shows most lines as considerably more intense near the cathode, as a result of cathode layer enrichment. It may be compared with Plate 3(1), which shows spectra of the same sample recorded by arcing 50–100 mg of specimen, using anode excitation. The longitudinal intensity distribution here is very nearly uniform for almost all lines (except ion lines, which show pole effects).

Mannkopff and Peters have reported a cathode layer enrichment effect for many elements. Zn, Cd, and Cu showed a cathode enrichment intensity of 5–10×, and cathode layer enrichment was reported as very marked in most elements of the first three vertical columns, as well as for elements such as Si, Sn, Pb, Bi, Fe, Ni, and Co. In general, elements of relatively low ionization potential exhibit cathode layer enrichment to the greatest extent, whereas it is poorly developed in elements of high ionization potential, such as B and Hg. This is due to the limited ionization and consequent small amount of ion migration toward the cathode.

Cathode layer enrichment is most marked when the arc is essentially a carbon arc in air. Under these conditions the highest possible temperature and consequently the highest degree of ionization are attainable. A relatively long ($\sim$ 10 mm) arc gap is also more conducive to the development of cathode layer enrichment. Because the presence of those elements with an ionization potential less than about 10–11 volts lowers the temperature, the quantity of material entering the arc column must be kept at an absolute minimum. This may be done in an analysis by loading less than about 10 mg of sample in the *cathode*. Because rate of release (volatilization) from the anode is excessively rapid, cathode layer enrichment tends to be destroyed even if only 5–10 mg are arced from the anode.

Cathode layer enrichment is lowered very considerably in the presence

of the alkali metals. Because of their low ionization potentials, these elements decrease arc temperature and consequently ionization is lowered. Compare the intensity distribution of Si 2528 in (a) and (b) of Fig. 8–4, for example. A specimen of silicate rock was arced using a typical small-diameter cathode. The longitudinal intensity distribution during the early arcing period is shown in (a); here there was a relatively high concentration of sodium and potassium. In (b), taken at a later stage of arcing, sodium and potassium had volatilized and the arc temperature increased considerably. Those who have recommended the use of cathode layer excitation in preference to anode excitation have asserted that two advantages accrue from its use. First, an improvement in sensitivity and second, a greater quantitative reproducibility.

A greater *absolute* sensitivity* is undoubtedly attainable when using cathode layer excitation, as may easily be demonstrated by arcing impure electrodes or very small quantities of material. If, however, the analyst has at his disposal sufficient material (50–100 mg), the limit of detection (relative sensitivity)** obtained by arcing a larger specimen with anode excitation appears at least equal to that obtained when cathode layer excitation and a smaller specimen are used. This has been the experience of Pierce, Torres, and Marshall (1940) and Ahrens and Liebenberg (1946). It is not easy to make a comparison of the two methods by means of published data because many operating factors (plate types, base material, conditions of excitation, and other details) differ so widely. In any case, it is difficult to estimate accurately the concentration at which a given line disappears into background. However, some indication that the relative sensitivities are of the same magnitude may be found in Table 5–5, a comparison of results published by Mitchell (1946), who employed cathode layer excitation, and Ahrens and Liebenberg (1946), who used anode excitation. Mitchell used Ilford Special Long Range Spectrum plates and Ahrens and Liebenberg used Ilford Iso-Zenith and Ilford Extra Sensitive plates.

In general, magnitudes for the limits of detection for the two respective methods are similar, that is, they differ within a factor of five. Personal observation has indicated that anode excitation may in general be more sensitive for the very volatile group of elements provided a large specimen is loaded into a fairly deep cavity and these elements are made to distill off relatively slowly at a low amperage ($\sim$ 3 amp) for a long time.

A further comparison is made in Table 5–6, which has been taken from

* Smallest detectable weight of element, expressed either in milligrams or micrograms.

** Lowest detectable concentration, expressed either as percentage or parts per million.

Table 5-5

Element	Mitchell (1946)		Ahrens & Liebenberg (1946)	
	Line used	Limit of detection %	Line used	Limit of detection %
Ag	3280	0.001	3280	0.0001
Ba	4934	0.0005	4934	0.0002
Be	3131	0.001	3130	0.0002
Co	3453	0.0002	3453	0.0005
Cr	4254	0.0001	4254	0.0001
Ga	2943	0.0001	2943	0.002
La	3337	0.003	3949	0.002
Li	6707	0.0001	4603	0.0006
Mn	4030	0.001	4034	0.0003
Mo	3170	0.0001	3170	0.0005
Ni	3414	0.0002	3414	0.0001
Pb	2833	0.001	2833	0.001
Rb	7800	0.002	4201	0.002
Sn	2840	0.0005	3262	0.002
Sr	4607	0.001	4607	0.0004
Tl	2767	0.005	3775	0.00003
V	3185	0.0005	3185	0.002
Y	3327	0.003	3327	0.001
Zn	3345	0.03	3345	0.005
Zr	3392	0.001	3438	0.002

Ahrens and Liebenberg (1946). Various materials have been analyzed by means of cathode layer and anode excitation; the presence of elements detected by either of these methods is indicated by a + in Table 5–6. (All place-names refer to South Africa.) Inspection of this table again indicates that the relative sensitivities of anode and cathode layer excitation are about the same for most elements in various matrices.

The reputedly greater accuracy of cathode layer excitation has not been generally verified. Because cathode layer excitation requires electrodes of very small diameter, however, a relatively smooth-burning arc may more often be obtained than in anode excitation, where relatively large electrodes are often necessary to obtain sufficient sensitivity. On the other hand, the rapid longitudinal change of line intensity and the high sensitivity of this longitudinal intensity distribution to a change of the excitation energy in the arc may impair quantitative reproducibility in the cathode layer arc.

Some laboratories concentrate on anode or perhaps cathode excitation and others invariably employ cathode layer excitation. Probably the best results are obtained if excessively rigid routines are not adopted. The analyst should be flexible in his approach and draw freely on different procedures as the need arises.

Table 5-6

Qualitative Analysis of Several Materials for Minor Constituents Indicating Comparative Sensitivities for Anode and Cathode Layer Excitation.

Specimen and Locality	Method	Elements																				
		Ag	Ga	Sn	Pb	Zn	Li	V	Mo	Ni	Co	Mn	La	Ba	Sr	Y	Sc	Zr	Tl	Cr	Be	Bi
Bushveld granite, Pretoria	A	+	+	-	+	-	-	-	-	+	-	+	+	+	+	+	-	+	+?	+	-	-
	C	+	+	-	+	-	-	-	-	+	-	+	+	+	+	+	-	+	+?	+	-	-
"Old granite," Johannesburg	A	+	+	-	+	-	+	+	-	+	+	+	-	+	+	+	+	+	+?	+	-	-
	C	+?	+	-	+	-	+	+	-	+	+	+	+?	+	+	+?	+	+	+?	+	-	-
Yellow shale clay, Grahamstown	A	+?	+	-	+	-	-	+	-	+	+	+	+	+	+	+	+	+	-	+	-	-
	C	+?	+	-	+	-	-	+	-	+	+	+	+	+	+	+	+	+	-	+	-	-
Fireclay	A	-	+	-	+	-	-	+	-	+	+	+	-	+	+	-	+	+	-	+	-	-
	C	-	+	-	+	-	-	+	-	+	+	+	-	+	+	-	+	+	-	+	-	-
Nontronite kaolinite, Kuruman	A	+	+	-	+	+?	-	-	-	+	-	+	+	+?	+	-	-	+	-	-	-	-
	C	-	+	-	-	-	-	-	-	+	-	+	+	+?	+	-	-	+	-	-	-	-
Nontronite kaolinite, Zoutpan, Cape Province	A	+	+	-	-	-	-	+	-	+	+	+	+	+	+	+	+	+	-	+	+?	-
	C	+	+	-	-	-	-	+	-	+	+	+	+	+	+	+	+	+	-	+	+?	-
Dolomite, Transvaal system	A	+	-	-	-	-	-	+	-	+	-	+	-	+	+	-	-	-	-	+	-	-
	C	+	-	-	-	-	-	+	-	+	-	+	-	-	-	-	-	-	-	+?	-	-
Surface limestone, Cretaceous system, Kareelaagte	A	+?	+	-	-	-	+	+	-	+	+?	+	-	+	+	-	+	+	-	+	-	-
	C	-	+	-	-	-	+?	+	-	+	+?	+	-	+	+	-	+?	+	-	+	-	-
Solids in solution, Crocodile River	A	+	-	+	+	-	+	+	+?	+	+	+	-	+	+	-	-	-	-	+	-	+
	C	+	-	+	+	-	-	+	+?	+	+?	+	-	+	+	-	-	-	-	+	-	+?
Solids in solution in spring water, Old granite	A	+	-	+	+	-	+	+	+	+	+	+	-	+	+	-	-	-	-	+	-	-
	C	+?	-	+?	+	-	+	+	-	+	-	+	-	+	+	-	-	-	-	+	-	-
Solids in solution, 'Six Mile' Stream	A	+	-	+	+	-	-	+	-	+	-	+	-	+	+	-	-	-	-	+	-	-
	C	+?	-	-	-	-	-	+	-	+	-	+	-	+	+	-	-	-	-	+	-	-
Pyroxenite, Bushveld Igneous Complex	A	-	+	-	-	-	+?	+	-	+	+	+	-	+	+	-	+	-	-	+	-	-
	C	-	+?	-	-	-	+?	+	-	+	+	+	-	+	+?	-	+	-	-	+	-	-
Olivine basalt, Kruger National Park	A	-	+	-	-	-	+	+	-	+	+	+	-	+	+	-	+	+	-	+	-	-
	C	-	+	-	-	-	+	+	-	+	+	+	-	+	+	-	+	+?	-	+	-	-

A = Anode excitation.
C = Cathode layer excitation.

In Table 5–7 several properties of anode and cathode layer excitation are compared.

Strock (1936b) gives an account of the use of cathode layer excitation and lists many references to papers which describe this method.

Much has been written, particularly in the 1930's, in support of cathode layer excitation, but less in defense of anode excitation. Because the advantages of cathode layer excitation as enunciated by its exponents do not appear so significant in the light of the comparisons drawn in this chapter, one is inclined to think that the cathode layer exponents have overstated their case.

5–7. The most sensitive lines of the elements. To establish the presence or absence of an element it is usually necessary to employ only one or two of the most sensitive lines. If these lines are absent, it is obviously unnecessary to look for other lines of the element unless there has been interference. Unfortunately, however, there is not always unanimity as to which lines are the most sensitive. Much depends, of course, on the equipment available and on the operating technique which has been employed. Theory has been an aid here, and Meggers (1941, a and b) has been able to predict from theory the most intense, and therefore the most sensitive, atom and ion lines, for the majority of the elements. His conclusions are a useful guide.

Several books of wavelength tables give lists of the sensitive lines of most elements, but the author feels that the inclusion of a set of tables as arranged in this book should be useful for several reasons (see Appendix I). Apart from a significant disagreement among authors of wavelength tables as to the actual lines listed, there are quite frequently discrepancies between these lists and the observations of practicing spectrochemists. Scandium is one example. The experience of many analysts has been that Sc 4246 is the most sensitive line of scandium, but in some tables it is listed as one of the less sensitive lines and in others it has been omitted. In compiling these tables, every attempt has been made to select the most sensitive lines from the widest possible range of sources — papers, wavelength tables, personal observations, and theory. Only 2–4 lines are given for each element; these should serve adequately for most qualitative analyses. No claim is made that the lines given are the most sensitive for every element, because for some elements information is generally lacking on the relative sensitivities of their most intense lines.

In the tables in this book, the 2–4 most sensitive lines for each element are given first, together with their excitation potentials. Those lines which have been underscored thus _____ or thus _ _ _ refer respectively to the most sensitive atom and ion lines as predicted by Meggers (1941,

Table 5-7

Absolute sensitivity:	Higher in cathode layer excitation.
Limits of detection: (relative sensitivity)	Approximately the same. Some very volatile elements may be more sensitive in anode excitation.
Electrode impurities:	More readily revealed in cathode layer excitation.
Time required for complete consumption of sample:	Volatilization much slower from cathode; consequently time of arcing longer when cathode layer excitation employed.
Selective volatilization:	Usually more marked in anode excitation. Choice of internal standard therefore sometimes more difficult.
CN emission:	More marked in cathode layer excitation. CN emission can be quenched completely in the presence of alkali vapor when anode excitation is employed (Section 10-2).
Longitudinal intensity distribution:	Nearly uniform in anode excitation except for ion lines which show "pole" effects. In cathode layer excitation line intensity increases sharply near cathode.
Temperature, degree of ionization, and excitation level:	Temperature of cathode layer arc greater as it is more nearly a carbon arc in air (Section 3-4). Consequently higher degree of ionization; intensity of lines of relatively high excitation potential enhanced.
Influence of compositional change on longitudinal line intensity distribution:	Longitudinal line intensity distribution is very sensitive to compositional changes in cathode layer arc (Section 8-3).

a and b). If no underscore is present, it has either been impossible to make the theoretical prediction as yet, or the wavelength of the line is outside the normal working range. In a very few cases theory does not seem to have accorded with practice, and these lines are not listed. In general the lines predicted from theory appear to be the true *raies ultimes*. The intensities of the other sensitive lines listed are rough indications of the order of their relative sensitivities. It was felt that qualitative analysis would be facilitated by arranging the most sensitive lines in such a way that when a sensitive line was consulted the wavelengths of all possible interfering lines could be seen immediately. For this reason the most sensitive lines are given again in the body of the table, together with all lines within ±0.4–0.5A which are excited in the arc. For this purpose the M. I. T. Wavelength Tables (Harrison, 1939) have been consulted, and the wavelengths, intensities, and symbols are as given there unless otherwise stated.

For some elements, spark (ion) lines are usually the most sensitive in the arc. Sc 4246 and several rare earth ion lines are good examples. It must of course be realized that the relative intensities of lines are sensitive to conditions of excitation and may consequently vary with different types of materials. This applies in particular to a comparison of atom and ion lines. Thus, the very sensitive low temperature calcium line Ca 4226 is much more intense and consequently much more sensitive than Ca 3933, the most sensitive ion line in the spectra of minerals rich in alkali metals $\left(\frac{I \text{ Ca } 4226}{I \text{ Ca } 3933} > 2.0\right)$. If the arc temperature is high, as for example when impure electrodes are arced, Ca 3933 is more intense than Ca 4226 $\left(\frac{I \text{ Ca } 3933}{I \text{ Ca } 4226} > 2.0\right)$ and the ion line is more sensitive.

The excitation potentials given in the tables include atom and ion lines. For the latter, these potentials refer to the true excitation potential of the line, that is, the energy required by the ion for the emission of the line, and not to the *total* excitation potential (Section 3–5). The total excitation potential for ion lines is sometimes used, but for analytical purposes may convey an erroneous impression of the energy characteristics of a line.

Although the wavelength tables given in this book suffice for many purposes of qualitative analysis, a general and reasonably complete book of wavelength tables is necessary as well. For the analysis of the spectra of such complex materials as minerals, rocks, soils, and related materials, the M. I. T. Wavelength Tables are a necessity. Fairly complete but less detailed are the tables of Kayser and Ritschl (1939) and the earlier tables of Kayser and co-workers.

An examination of the very complex spectra of rare earth mixtures calls for special study. For this purpose, detailed tables on the individual rare earth elements are of value. Gatterer and Junkes (1945) have published tables and charts on the rare earth spectra. These authors provide many references to other publications giving wavelength tables of rare earth lines. A few of the weaker rare earth lines listed in the M. I. T. Tables are incorrect, according to Smith and Wiggins (1949). They point out that the source of error was evidently the presence of some other rare earths in the compounds of those that were believed to be pure when analyzed. Smith and Wiggins give examples of some incorrectly labelled lines and also provide the most recent information on the most sensitive lines of the rare earth elements. Brode (1943) and Harrison, Lord, and Loofbourow (1948) give bibliographies on wavelength tables.

In addition to tables, various spectrum charts of mapped enlargements which facilitate qualitative analysis are available for the analyst. The enlargement of the R. U. powder spectrum is an example, and Brode (1943) gives an enlargement of the iron spectrum on which the positions of many relatively sensitive lines of different elements are marked.

Some indication of the sensitivity of spectrochemical analysis has been given in Table 5–5. Harvey (1947), Claffy (1947), Standen (1944), van Tongeren (1938), De Azcona (1941) and Harrison, Lord and Loofbourow (1948) provide considerable information of this type. Further data on the spectral sensitivities of each of the elements may be found in Part II of this book.

When comparing sensitivities, some consideration should be given to the sizes of the spectrographs employed.

Harrison, Lord, and Loofbourow (1948, Chapter 15) point out the importance of the effect of varying dispersion on the detection limit (relative sensitivity). Whereas the absolute sensitivity depends on the light-gathering power of the spectrograph and the line-background intensity difference, detection limit depends almost entirely on the latter. With increasing dispersion, background intensity is dissipated over a greater plate length, whereas line intensity remains very nearly the same. Provided, therefore, that a large quantity of specimen is available, the greatest possible relative sensitivity is attained by giving a very long exposure (several superimposed ones if necessary) on an extremely large spectrograph. The use of a high-contrast emulsion helps to increase line-background intensity difference. It is of course not common practice to employ such methods for general qualitative analysis, but for those special purposes where the lowest detection limits are sought, these techniques are useful. Usually a three-fold increase in dispersion increases relative sensitivity by one order of magnitude.

Use may also be made of inert atmospheres for lowering the general level of background intensity. Thus, not only do A and He clear CN emission (Section 10–2) but in their presence the intensity of background radiation due to oxidation may be lowered. According to Vallee, Reimer, and Loofbourow (private communication), working in the Biology and Physics Departments, M. I. T., He is much more effective than A in this respect. Line intensity is also usually weakened, but in many instances the "signal-to-noise" ratio is increased; this sometimes makes it possible to lower the detection limit considerably. The use of such atmospheres creates an energetic environment that is different from that of the arc in air and appears to favor the emission of ion lines.

5–8. Methods of identifying elements. As it has been discussed in some detail in several other works, line identification will be described only briefly here. When an analyst is desirous of identifying one or perhaps a very few elements in a specimen, a quick identification can usually be made by recording the spectra of the elements sought adjacent to that of the unknown, using a Hartmann diaphragm. The Hartmann diaphragm, which is made to replace the reducing wedge controlling slit length, has three or more apertures 1–2 mm in length. By its use several successive spectra may be recorded without moving the plate. The racking down of the plate holder always entails the possibility of lateral displacement between successive spectra. The presence or absence of the strongest lines of the element sought may be ascertained by inspection of the spectra thus obtained. Plate 1(c) shows four spectra: (a) cadmium, (b) *sphalerite* (*zinc blende*) — light specimen, (c) *sphalerite* — dark specimen, and (d) *indium*. It was desired to know whether or not these two specimens of *sphalerite* contained cadmium or indium. The strongest lines of indium and cadmium are present in both *sphalerite* specimens, as may be seen in Plate 1(c). The strong indium and cadmium lines are themselves easily identified by reference to mapped enlargements of the spectra of different elements.

Such a simplified procedure cannot ordinarily be adapted to the qualitative analysis of the complex spectra of most minerals, rocks, and soils and either of two general methods is employed. One necessitates the measurement of the dispersion of the spectrograph, the accurate location of lines on the spectrogram, and sometimes wavelength. In the other, use is made of key plates and enlarged charts on which the sensitive lines of many elements have been marked.

In the first method an iron arc spectrum is photographed adjacent to and slightly overlapping the spectrum of the unknown. A 3-amp arc exposed for 5 seconds in the region 3000–5000A and about 20 seconds for the range 2000–3000A is usually satisfactory for this purpose. The iron

arc spectrum is used for the determination of dispersion (unless already known), as a reference spectrum for lines of known wavelength, and in general for finding one's way around the spectrogram. Consider the analysis of *sphalerite* again — the analyst desires to know whether indium and cadmium are present. An inspection of tables which list the most sensitive lines (for example, those given in this book) give In 3256 and Cd 3261 as two very sensitive lines. From an inspection of mapped enlargements of an iron spectrum (a valuable requisite for any laboratory) the general region where In 3256 and Cd 3261 are located is found and in it two (or more) iron lines of known wavelength are identified. Their separation is measured accurately in mm. If λ_1 is the wavelength of the iron line of longer wavelength and λ_2 that of the shorter and if their separation is d mm, dispersion is given by $\frac{\lambda_1 - \lambda_2}{d}$ A/mm. An eyepiece magnifier with an internal scale or a projected enlargement of the spectra on a screen is employed to measure line separations.

A calculation is then made of the distance of the line sought (In 3256 or Cd 3261) from one of the iron lines. If λ_r and λ_a are the wavelengths of the reference (iron) and analysis lines respectively and if the dispersion is 5A/mm, the distance of λ_a from λ_r on the spectrogram is given by $\frac{\lambda_a - \lambda_r}{5}$ mm if $\lambda_a > \lambda_r$, or $\frac{\lambda_r - \lambda_a}{5}$ mm if $\lambda_r > \lambda_a$. The spectrogram is then critically examined for the presence of a line at the calculated distance away from the reference line.

When undertaking a qualitative analysis, beginners have a tendency to look for lines rather than elements, that is, when confronted with the complex spectrogram emitted by a mineral, rock, or soil they often attempt the identification of every line. In this process they frequently find almost every element and may become confused when attempting to use the main body of the M. I. T. tables. Their object should always be to analyze element by element, using only a couple of the most sensitive lines for identification and ignoring the distracting presence of hundreds of other lines. Experienced analysts usually encounter no difficulty when using the main body of the M. I. T. tables.

If the wavelength of a certain line is to be determined, it is measured as follows. The dispersion of the spectrograph at the approximate wavelength of the unknown line, λ_u, is determined unless already known. The distance of the unknown line to a neighboring iron reference line is measured ($= d$ mm). If the dispersion is 5A/mm and the wavelength of the reference line is λ_r, the wavelength of the unknown is

$$\lambda_u = \lambda_r + (5 \times d)\, A, \text{ if } \lambda_r < \lambda_u,$$

or $$\lambda_u = \lambda_r - (5 \times d)\, A, \text{ if } \lambda_r > \lambda_u.$$

Reference to the M. I. T. tables should show to which element the line belongs.

If prism optics have been used and if a closely located reference line has not been available, the simple interpolation calculation cannot be employed because of the rapid change of dispersion with wavelength. For the same reason, the lines used for the determination of dispersion must be closely spaced when prism optics are employed. The approximate tolerance is 20A at 6000A, 10A at 3000A, and 3A at 2100A. If the lines are widely separated, more complex relationships are required for the determination of wavelength. This is discussed in some detail by Sawyer (1944) and also by Harrison, Lord, and Loofbourow (1948). It is very rare that recourse must be made to the use of more complex relationships for wavelength measurement in the analysis of minerals, rocks, and soils. Even if an iron line is not nearby, other lines of known wavelength invariably can be used as reference lines.

Most rock and soil specimens and a high proportion of minerals carry a sufficient concentration of iron to produce many iron lines, and it is then unnecessary for the iron arc spectrum and that of the unknown to overlap. Wavelength measurements can usually be made with the aid of these iron lines or the lines of such common elements as Ca, Mg, Mn, and Ti, all of which are easily recognizable once the analyst has had some experience with them.

The use of spectra emitted from the specimen itself rather than those of an iron arc is in general preferable for wavelength measurement. Often during analysis the plateholder is racked down, either continuously or at definite intervals. It is then impossible to use one reference iron spectrum to measure the wavelengths of lines which appear in the successive spectra because there is no overlapping. Furthermore, if lines emitted by the sample are used as reference lines, lateral displacement of the plate cannot introduce error.

A second general method of identifying elements employs reference or key plates in conjunction with a comparator. A reference plate contains the spectrum of a synthetic powder which has traces of many elements in sufficient concentrations to record the sensitive lines of each. R. U. (raies ultimes) powder is such a powder; it is obtainable from Adam Hilger, London, or from the Jarrell-Ash Company, Boston. An enlargement of the R. U. powder spectrum, on which are marked the sensitive lines of all the elements in the R. U. powder, is also available. With the aid of this enlargement, an analyst can identify and mark the sensitive lines on a key plate he has prepared either from an R. U. powder specimen or from similar

material. On this key plate an iron arc is photographed. The unknown plate, which also carries the iron arc spectrum, can then be analyzed in a comparator. Key and unknown plates are aligned and the spectra brought into juxtaposition by matching the respective iron spectra. In this position the presence or absence of various elements can usually be ascertained without having to make wavelength measurements. This general procedure is very rapid and convenient, but if doubt arises the identity of a line must be established by wavelength measurement.

Because of variable dispersion in a prism, a comparator + key plate procedure is of particular use for scanning spectrograms taken on a prism spectrograph.

5–9. Slit illumination for qualitative analysis. Almost any system of illumination may be employed for qualitative analysis. As a rule, however, high intensity of illumination is desirable, for which purpose a single spherical condenser of short focal length is frequently employed. Such a lens brings the source into focus at the slit. Another method of slit illumination quite commonly used is type 4 in Section 9–3.

Because of the great complexity of the spectra emitted from minerals, rocks, and soils, a very high resolution is desirable and consequently a relatively narrow slit (0.01–0.02 mm) should be employed. Up to extremely narrow slit widths, resolving power increases with decrease in slit width; intensity of illumination also decreases and a compromise should be made. For a given spectrograph and wavelength an optimum slit width may be determined. In general, however, the widths given above are satisfactory.

Stockbarger and Burns (1933) discuss resolving power in relation to various methods of illumination.

To overcome chromatic aberration, achromatic lenses (quartz-fluospar or quartz-rocksalt) must usually be employed. These are very expensive and the cheaper aluminized concave mirror may be substituted to attain achromatism.

5–10. Color of the arc image. Sometimes information can be obtained about the composition of a sample merely by an inspection of the color of an enlarged image of the arc. If a spherical condenser of short focus has been used, the arc image on the slit can be examined, or if other methods of illumination have been employed, the image on a positioning screen is examined. This color analysis is of course only a modification of a flame test but may be of considerable value to the analyst.

When a knowledge of only the major constituents in a sample is desired, recourse need not always be made to the recording of the spectrum because the arc color is sometimes a sufficiently positive test. Often also it is of

value to know the major phases of vaporization in the arc, and this can frequently be done by watching its color changes. For example, an analysis might be required of Pb, Ga, Rb, and Tl in *feldspar*, of which these elements are typical minor constituents. Several of the most sensitive lines of these elements are located in CN bands (Section 10–2) which cause interference unless suppressed. Pb, Ga, Rb, and Tl are volatile elements and so are the alkali metals in whose presence CN emission is very effectively quenched. The arc is allowed to run therefore until the yellow flame-like appearance (due to sodium in *feldspar*) begins to thin, and the exposure is stopped. If the exposure is continued for a longer period, excessive CN emission develops and spoils the test; the correct exposure is "timed" by the disappearance of the yellow color from the arc. See also observations by Fast (1950) on analysis of potassium in the presence of interference from iron.

Table 5–8 (adapted from Peterson, Kauffman and Jaffe (1947) lists the colors that are observable in the arc image when various elements are present.

Table 5-8

Element	Color of arc image	Element	Color of arc image
		Nb	Blue with red fringe
Al	Greenish blue	Nd	Light orange-red
Sb	White fumes	K	Bluish-white
Ba	Green	Pr	Greenish-gray
Be	Greenish blue	Sc	Light orange
B	Green	Sm	Red
Ca	Orange	Ag	Green
CaF_2	Canary yellow	Na	Yellow
		Sr	Red
Cr	Green	Ta	Blue with red fringe
Cs	Bluish white	Tl	Green (very intense)
Cu	Green	Ti	White
Fe	Blue with yellowish white fringe	U	Bluish white
Li	Red	W	Blue when current is reduced
Mg	Green	Y	Red
Mo	Blue	Zr	White flashes

Table 5-9

Visual (spectroscopic) sensitivities

Element	λ	Sensitivity (%)
Ag	5465.4 5209.0	.001 - .01
Al	3961.5 3944.0	.001 - .01
Au	4792.0	0.5
B (BO)	diffuse BO bands	>1
Ba	5535.5 4934.1 4554.1	.0001 - .001
Be	4572.7	.1 - 1
Bi	4722.2	.001 - .01
Br(BaBr)	5360.1 5208.2	barely perceptible
Ca	4226.7	.0001
Cd	5085.8 4799.9 4678.5	.001 - .01
Ce	5512.1 4628.2	no standards, perhaps 0.1 - 1
Cl(CaCl)	6211.6 5934.0	no standards, perhaps 1
Co	4867.9 4840.3 4813.5 4792.9	0.1 - 1
Cr	5208.4 5206.0 5204.5	.001 - .01
Cs	4593.2 4555.5	no standards
Cu	5218.2 5153.3 5105.6	.001 - .01
Dy	4957.4	no standards, perhaps .1 - 1
F(CaF)	6064.4 5291.0	.001 - .01
Fe	5371.5 5328.4 5269.5	.1
Ga	4172.7	.001 - .01
Gd	5155.8 5103.5 5015.0	no standards, perhaps .1 - 1
Ge	4683.0 4226.7	? (CN Interference)
Hf	4093.2	no standards
Hg	5460.7	no standards
In	4511.3	.001
Ir	5449.5	1
K	7699.0 7664.9 6939.0 6911.3	.5
La	4921.8 4899.9	.1
Li	6707.9	.00001
Mg	5183.6 5172.9 5167.3	.001 - .01
Mn	4823.5 4783.4 4766.4 4762.4 4754.1	.001 - .01
Mo	5570.3 5533.0 5506.5	.001 - .01
Na	5895.9 5889.9	.0001 - .001
Nd	5319.8 5293.2	no standards, perhaps .1 - 1
Ni	5476.9	.01 -.1
Os	4420.4	.1 - 1
Pb	4057.8	.001 - .01
Pd	5295.6 5163.8 4212.9	.01 - .1
Pr	5110.8	no standards
Pt	5059.5	.1 - 1
Rb	6298.6	no standards
Re	5275.5 4889.2	no standards
Rh	5599.4 4374.8	.1 - 1
Ru	5171.0 4554.5	.01 - .1
Sb	4033.5	>5
Sc	5087.0 5085.5 5083.7 5081.6	.005 - .05
Si	3905.5	1 - 10
Sm	4883.9 4815.8 4760.3	no standards, perhaps .1 - 1
Sn	4524.7	.1 - 1
Sr	4607.4 4215.5 4077.7	.0001 - .001
Ta	5402.5 4812.7	.5
Th	6408.6	.5
Ti	5014.3 5007.0 4999.5 4999.1 4891.7	.001 - .01
Tl	5350.5	.001 - .01
U	5915.4	.5
V	4881.5 4875.5 4864.8 4851.5 4832.4 4827.4	.01 - 1
W	5224.7 5053.3	.1
Y	Y 5087.4 YO 6132.1 YO 5972.2	.001 - .01
Zn	4810.5 4722.2 4680.1	.001 - .01
Zr	4815.6 4772.3 4739.5 4710.0 4687.8	.01

Silicon imparts no color to the arc and beginners should feel no concern when as a result of this lack of color no material appears to be entering the arc column. (Additional reference, Mott (1920).)

5–11. Visual (spectroscopic) analysis. Since the large-scale adoption of photographic emulsion for recording spectra, visual spectrochemical analysis has been used to a very limited extent. In industry, the *steeloscope* (Twyman, 1941, pp. 275–278) is sometimes employed for the analysis of metals and alloys and in universities small spectroscopes are often used for demonstration purposes. As a source of excitation for visual spectrochemical analysis early workers frequently employed the flame. Recently, however, the d.c. arc has been used as a source for the visual spectrochemical analysis of minerals and some other materials. (Peterson, Kauffman, and Jaffe, 1947; Gabriel, Jaffe, and Peterson, 1947; Jaffe, 1949.) Although such methods of analysis have limitations when compared with the use of the photographic emulsion, they offer certain definite advantages.

The visual method is extremely fast. The mineralogist will find it very handy for some purposes in determinative mineralogy. As one example, it is possible to distinguish quickly between *chlor-apatite* and *fluor-apatite*. (Section 14–2.) The cost of a suitable spectroscope is only a fraction of the cost of a satisfactory spectrograph.

The analyst who views his spectra visually is apt to learn quickly about the behavior of the arc, and selective volatilization (Chapter 6) in particular. He is ever aware of the selective waxing and waning of line intensities.

Table 5–9 provides information on lines and bands which have been employed for visual spectrochemical analysis with the d.c. arc. Approximate sensitivities are also given. These data have very kindly been placed at the disposal of the author by Mr. Howard W. Jaffe of the U. S. Bureau of Mines.

CHAPTER 6

SELECTIVE VOLATILIZATION

6–1. General. When a specimen which contains several elements present either in elemental or combined forms is arced, each element tends to volatilize selectively from the electrode cavity into the arc column. Selective volatilization, known also as fractional distillation or selective vaporization, may be observed in many excitation sources but is most characteristic of the d.c. arc. This is particularly true when anode excitation is employed. An adequate understanding of its importance cannot be overemphasized, particularly for the development of accurate quantitative methods.

As early as 1908, Eberhard refers to selective volatilization and mentions the late appearance of the spectra of scandium and sundry rare earths when minerals and rocks are arced. In more recent years Mannkopff and Peters (1931) have discussed selective volatilization in their publication on cathode layer excitation and many authors have subsequently referred to this phenomenon.

To observe selective volatilization, it is necessary to record change of line intensity with regard to time during the whole period of arcing. This is done by racking down the plateholder stepwise at definite intervals (10–30 seconds for example), or by moving the plate continuously at a slow rate by means of a geared motor which can operate at different speeds. If microphotometric measurements are to be made, it is more convenient to move the plateholder stepwise. The data used in constructing the various volatilization curves in this book are from plates that have been moved stepwise.

A graphical representation of line intensity vs each interval of time is a convenient way of portraying selective volatilization. Fig. 6–1 shows a typical family of selective volatilization curves, somewhat idealized. Anode excitation (7 amp) was used and the elements examined were present in a matrix whose composition roughly approximated that of a silicate rock. The curves refer to an untreated specimen, free from admixture with powdered carbon. Selective volatilization can conveniently be observed by arcing a silicate in an electrode type similar to No. 2 in Fig. 5–2, because a single globule or bead is usually formed.

Fig. 6–1 shows that each element has a characteristic manner of volatilization with a peak intensity of emission different from any of the others. The intensity peaks may be very flat or have sharp profiles; good examples of both are the volatilization curves shown in Fig. 7–1. The curves shown

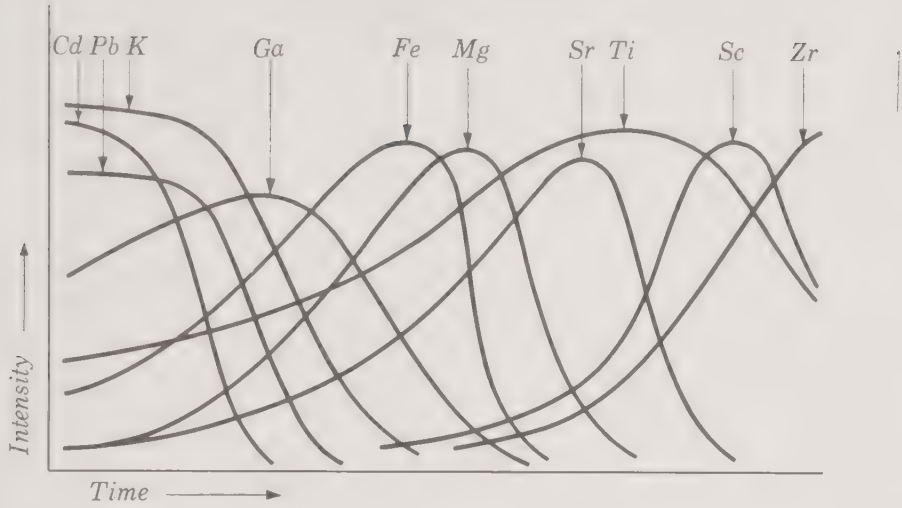

Fig. 6–1. Family of volatilization curves illustrating selective volatilization (fractional distillation). Somewhat idealized.

in Fig. 6–1 refer to the volatilization of the elements as a whole. If an attempt is made to employ such curves when using lines of large energy difference (an ion and a low temperature atom line) and if the composition of the arc column changes markedly with time, apparent discrepancies due to differences of the excitation characteristics of the lines will result.

6–2. Boiling points and selective volatilization. Once the arc has been struck, the specimen frequently forms a molten globule unless some procedure (carbon admixture for example) has been used to prevent globule formation. At the liquid-gas boundary equilibrium exists between liquid and gas phases. Here the vapor pressure, and consequently the boiling point, of the element or compound in the melt is important in controlling the rate of release (volatilization) of the element from the liquid phase.

Table 6–1 gives the boiling points of several elements and their respective oxides. Most of this information has been obtained from the Handbook of Chemistry and Physics (1947) and also from Richardson (1937). In Table 6–1, the lower case letters *s*, *d*, *ca*, and *m. pt.* refer respectively to sublimes, decomposes, calculated, and melting point. Where a boiling point temperature has not been obtainable, that of the melting point has been given as a rough measure of the minimum value of the boiling point.

Attempts have been made to correlate boiling point and vapor pressure data with the order of volatilization. In general there is a sympathetic variation between rate of volatilization and boiling point, although the relationship is not always simple. In Fig. 6–1, for example, the typically volatile elements, Pb, Cd, and Ga, the oxides of which have relatively low

Table 6-1

Boiling points of elements and some stable oxides in ^{o}C.

Ag	1950	Ga_2O_3	m.pt. 1900	P_2O_5	s.350
Ag_2O	d > 300	Ge	2700	Rb	700
Al	1800	GeO_2	m.pt. 1100	Rb_2O	d. 400
Al_2O_3	2250	Hf	3200	Rh	4500
As	s.615	HfO_2	5400	Ru	4900
As_2O_3	s.190	Hg	357	Sc	2400
Au	2600	HgO	d. 500	Sc_2O_3	4450
Ba	1140	In	1450	Si	2600
BaO	ca.2000	In_2O_3	d. 850	SiO_2	2230-2590
Be	1530	Ir	4400-5300	Sr	1150
BeO	ca.3900	K	760	SrO	m.pt. 2430
Bi	1470	La	1800	SnO_2	d. 1130
Bi_2O_3	1890 (?)	La_2O_3	4200	Ta	6000
B	2550	Li	1610	Ta_2O_5	d. 1470
B_2O_3	1230	Li_2O	m.pt. 1700	Te	1390
C	4200	Mn	1900	TeO_2	s. 450
Ca	1240	MnO	m.pt. 1650	Tl	1460
CaO	2850	Mn_3O_4	m.pt. 1705	Tl_2O	1080
Cd	767	Mg	1110	Th	5200
CdO	d.950-1000	MgO	m.pt. 2500-2800	ThO_2	4400
Ce	1400	Mo	3700-5700	Ti	5100
CeO_2	m.pt. 1950	MoO_3	s.	TiO_2	d. 1640
Co	2900	Na	880	V	3000
CoO	m.pt. 1935	Na_2O	s.1275	V_2O_5	d. 1750
Cr	2200	Nb	3700	W	5900-6700
Cr_2O_3	m.pt.1990	Nb_2O_5	m.pt. 1520	WO_3	s.
Cs	670	Ni	2900	Y	d. 2500
Cs_2O	d.360-400	NiO	3380	Y_2O_3	m.pt. 2400
Cu	2310	Os	5500	Zn	907
CuO	d. 1030	Pb	1610	ZnO	s. 1800
Fe	3000	PbO	m.pt. 890	Zr	5050
FeO	m.pt. 1420	Pd	2540	ZrO_2	5000
Fe_2O_3	m.pt. 1565	Pt	4300		
Ga	2000	P	280		

boiling points, emit their peak line intensities early, whereas those elements which have oxides of high boiling point, namely Sc, Ti and Zr, are typically involatile. The stability of a compound in the electrode cavity is frequently a complicating factor. In these circumstances one is not sure which boiling point data to use. In silicates it is common to consider the boiling points of the oxides of the elements, but there may be partial reduction to the element. This in turn may be converted to carbides or nitrides at the high temperatures which prevail in the electrode cavity. Some elements readily form carbides under such conditions; reduction to element and carbide formation tends to occur where the molten material wets the carbon surface. When carbonates and sulphates are arced, CO_2 and SO_3, respectively, are released, and as a result these compounds usually behave as oxides. According to Rusanov (1945) sulfides and chlorides are volatilized as such; this probably applies to fluorides and chlorides as well. From phosphates, oxides of phosphorous are volatilized with little difficulty and the residual compounds probably behave as oxides.

If powdered carbon is mixed with the specimen, a far greater degree of reduction and carbide formation is to be expected. Richardson (1937) heavily diluted the oxides and salts of several elements with carbon and was able to show that where the boiling points of carbides of the elements were known, the times of appearance of their respective spectra could be correlated with their boiling points. Using this information, he was able to determine the boiling points of several elements which had been imperfectly known.

Rusanov (1943) has examined the volatility of many elements — as metals, sulfides and oxides — and has prepared tables of volatilities. Table 6–2 gives the volatilities for elements, and their sulfides and oxides. The data for elements and sulfides are as given by Rusanov, but data on the oxides are based chiefly on observations made by Mrs. L. G. Gorfinkle and the author at the Cabot Spectrographic Laboratory, M. I. T. These observations do not always agree with those of Rusanov. For example, Rusanov lists In, Tl, Cu, and Ga as of the same general volatility as Fe, Ni, and Co. This is contrary to our experience, which has always shown Cu, Ga, and particularly In and Tl, as much more volatile than Fe, Ni, and Co. Our data are based on anode excitation but appear to apply reasonably well to cathode layer excitation. See observations by Preuss (1935), for example, who employed cathode layer excitation.

In general there is a relationship between boiling points of elements and compounds, and order of volatilization.

For convenience, the oxides can be divided into three main volatility groups: volatile, medium volatile, and involatile. Each main group can be subdivided as indicated in Table 6–2. Such divisions are somewhat arbi-

trary and the observations of different analysts are bound to show some disagreement. It is not always easy to differentiate accurately between elements of the same general volatility and, further, relative volatilities will be somewhat altered by different matrices and techniques of arcing. In the main, however, elements which are placed reasonably far apart should consistently show a considerable difference in volatility. The data given in Table 6–2 should be of some aid to the analyst in selecting an internal standard for quantitative analysis (Section 7–4).

Table 6-2

Order of volatilization of elements in the arc

As elements:	Hg > As > Cd, > Zn, > Sb $\geqq$ Bi, > Tl, > Mn, >Ag, Sn, Cu > In, Ga, Ge > Au > Fe, Co, Ni ≫Pt ≫Zr, Mo, Re, Ta and W.
As sulfides:	As, Hg > Sn, Ge $\geqq$ Cd > Sb, Pb $\geqq$ Bi > Zn, Tl > In > Cu > Fe, Co, Ni, Mn, Ag ≫ Mo, Re
As oxides: (Applies also to sulphates, carbonates, silicates and phosphates).	As, Hg > Cd > Pb, Bi, Tl > In, Ag, Zn > ¦ Cu, Ga > Sn > Li, Na, K, Rb, Cs > | Mn > , Cr, Mo?, W?, Si, Fe, Co, Ni > ¦ Mg > Al, Ca, Ba, Sr, V > Ti > |Be, Ta, Nb > Sc, La, Y and many rare earths > ¦ Zr, Hf

6–3. Elimination of selective volatilization. Analysts frequently attempt to decrease selective volatilization as much as possible, mainly because of its detriment to quantitative reproducibility.

Selective volatilization develops most readily under the following conditions of operation: (1) anode excitation, (2) low current (2–4 amp), (3) relatively large anode cavity, (4) the presence of an element of low ionization potential (hence a relatively cool arc), and (5) a graphite anode rather than one of carbon. Selective volatilization can consequently be decreased by loading the specimen into a small carbon *cathode* which is arced at a high amperage. The presence of a high proportion of admixed powdered carbon or ammonium salts smooths out selective volatilization differences quite considerably, particularly among the relatively involatile

elements. Thus Fig. 6–2 shows volatilization curves for silicon and beryllium. Intensity measurements refer to Si 2528 and Be 2494. (1) shows the curves when anode excitation and a relatively large anode are used and no carbon is added, whereas (2) and (3) show the curves when cathode excitation is used and 2 and 14 parts, respectively, of carbon have been added. In (3) selective volatilization is seen to be very nearly eliminated. Such addition of carbon does not, however, eliminate volatilization differences when one of the elements is very volatile.

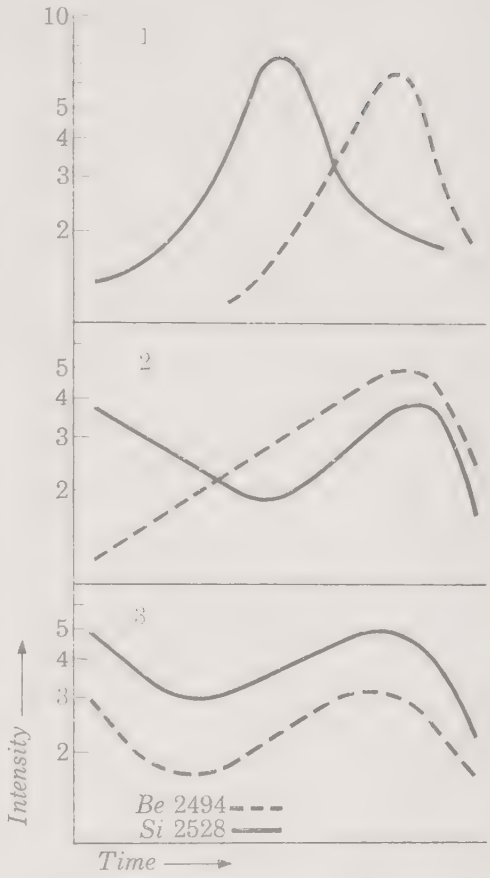

Fig. 6–2. Some volatilization curves for beryllium and silicon. Although beryllium is usually less volatile than silicon, in the presence of a high dilution of carbon powder (No. 3) volatilization differences are almost removed.

Selective volatilization may also be decreased by loading the specimen on a flat-topped electrode like type 1 (Fig. 5–1).

If all elements are converted into volatile forms, selective volatilization is not so marked. Conversion to volatile halides sometimes can be made by treatment with the appropriate acid, for example, HCl on carbonates and HF on silicates. NaCl, which is sometimes added as a buffer (Sec. 8–3), may react with the specimen in the electrode cavity, convert some elements to chlorides, and thereby partly eliminate selective volatilization. Selective volatilization is usually strongly in evidence when silicate minerals and rocks are arced. Silicates are, however, readily attacked by hydrofluoric acid and if the dried fluoride residues are arced, the spectra of all elements tend to be emitted intensely during the early period of arcing. Conversion to fluorides is sometimes useful for the complete analysis of *mica* and *feldspar*. The total arcing period is then rarely greater than about 1½ minutes if about 50–100 mg of sample is arced at 6–7 amp. An advantage of this procedure is the general absence of CN emission during the whole period of arcing (Section 10–2). When dried fluorides are loaded into the electrode cavity for analysis, it is desirable to heat the electrode in a flame for 10–20 seconds prior to arcing. Otherwise

the bulk of the fluorides is liable to be lost when the arc is started. An example of the use of dried fluorides is discussed in Section 10–2.

6–4. Some advantages of selective volatilization. Although all spectrochemists agree that the strong development of selective volatilization in the d.c. arc is a weakness of this source, it is not always realized that selective volatilization is often an aid to detecting and estimating some elements whose analysis lines are subject to interference. In Section 9–8 correction for line interference is discussed. Such correction is greatly facilitated when the elements sought and those causing interference have different volatilization rates. Consider the example of the interference of Mn 3256 with In 3256 in *lepidolite* (Section 9–8). Fig. 6–3 shows two volatilization curves, one for In 3256 and one for Mn 3256. It is quite clear that if the exposure is cut after some thirty seconds have elapsed, most of the total intensity of In 3256 will have been recorded, whereas only a fraction of the total intensity of Mn 3256 would then interfere. In a source in which selective volatilization is only slightly developed, interference from Mn 3256 would be much more likely to become excessive. (See also Section 12–2 and Fast (1950).)

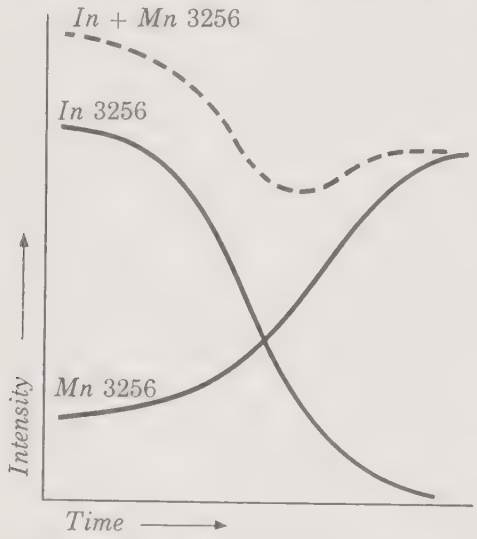

Fig. 6–3. These curves show that because indium is much more volatile than manganese, interference from Mn 3256 may be lowered considerably by exposing only the early period of arcing.

It may sometimes be desirable to suppress emission from an element which is likely to emit not only an extremely complex spectrum but also an intense general background due to continuous radiation. Background and a very complex spectrum lower sensitivity and cause interference. Minerals rich in Ta, U, Th, and the rare earths emit such disconcerting spectra. Scribner and Mullin (1946) describe a method of analysis of various elements in uranium (as the oxide) which is applicable to refractory oxides and minerals. Uranium is very involatile and 2.0% Ga_2O_3 is added to suppress its volatilization but not that of the more volatile elements sought. If the exposure is terminated before the main volatilization of uranium begins, the spectra of the elements sought can be examined in a relatively clean spectrum. Breckpot (1947) has described a method similar to that of Scribner and Mullin, but he

employed In_2O_3 and AgCl in place of Ga_2O_3. These techniques, which have been successfully employed for the analysis of several elements in refractory materials that emit very complex spectra and intense backgrounds, would be impossible if selective volatilization were less marked in the d.c. arc.

The advantages of selective volatilization in enhancing the sensitivity of very volatile and very involatile elements are illustrated by the observations of Preuss, De Rubies, and others, discussed in Section 5–5.

Mass spectrographers have been able to utilize selective volatilization in much the same way as have spectrochemists. Some of their observations are instructive. If in a mass spectrographic analysis, thermionic emission is used as a source of ions, elements are volatilized selectively as in an arc and interference from spectra of like mass-to-charge ratio can sometimes be removed. Thus Nier (1949) has been able to determine the ratio Sr^{87}/Sr^{88} in the presence of Rb^{87}, which interferes with the mass spectral "line" of Sr^{87}. Rubidium is more volatile than strontium and, after its complete volatilization, the ratio Sr^{87}/Sr^{88} can be determined. The complete volatilization of rubidium is ascertained by observation on the "line" due to Rb^{85}, which is a more abundant isotope than Rb^{87} and consequently produces a stronger "line." When this disappears, there will be no interference of Rb^{87} with Sr^{87}.

CHAPTER 7

GENERAL PRINCIPLES OF QUANTITATIVE ANALYSIS

7–1. Introduction. Shortly after the introduction of the spectroscope as an analytical tool in the middle of the nineteenth century, some speculation arose as to its possible quantitative application. For many decades, however, the use of spectrochemical analysis was almost entirely qualitative, although several observations were made on the progressive weakening of spectra with dilution. During the first quarter of this century the speculative glimmer was kept alive largely by the persistent appearance of publications by de Gramont, but even as late as 1924, Löwe was to refer to spectrochemical analysis as a "forgotten method" (see Meggers, 1946). At about this time Gerlach introduced the principle of internal standardization which in a modified form has been incorporated into the most accurate methods of quantitative analysis. Soon emission spectrography was to find wide application in quantitative analysis; some of the earliest large-scale quantitative investigations were made by the Goldschmidt school of geochemistry at Göttingen in the early 1930's.

One noteworthy exception to the general lack of application of the spectrograph to the quantitative analysis of minerals and rocks until the end of the 1920's is a contribution by Eberhard (1908) on the geochemistry of scandium. Although he employed approximate semiquantitative determinations, he was able to show very clearly that scandium is not a particularly rare element and is present in detectable amounts in many rocks and common rock-forming minerals. His was a major contribution to the geochemistry of scandium and is a good demonstration of the fact that it is sometimes possible to obtain much valuable information on the distribution and abundance of an element even if only approximate determinations have been made.

7–2. Sample preparation and loading of electrodes. The discussion on sample preparation and loading of electrodes in Chapter 5 applies also to quantitative analysis. The same electrode shapes and sizes are usually used, but if the elements sought are not at very low concentrations it is generally advantageous to arc a smaller weight of sample in a small diameter electrode. The arc burns more smoothly and reproducibility is usually improved. These comments on a possible reduction of electrode dimensions do not of course apply to cathode layer excitation, where a very small diameter cathode must be used for both qualitative and quantitative

analysis. One unfavorable characteristic of the d.c. arc source is the tendency of the arc to wander over the electrode surfaces. The use of a pointed upper electrode of carbon was recommended (Section 5–3) to reduce arc wandering over the upper electrode to a minimum. Dieke (1948) has shown the importance of oxidation on the electrode surface in controlling wandering of the cathode spot. He points out that these random fluctuations disappear almost completely when the arc source is in an atmosphere of nitrogen. Irregular arc wandering over the surface of the lower electrode holding the specimen sometimes causes uneven consumption of the crater walls and the sample, particularly when an electrode of relatively large diameter is used. As a result, quantitative reproducibility may be impaired and for this reason efforts have been made to ensure a uniform consumption of both electrode and sample. Jaycox and Ruehle (1940) have described a device for rotating the lower electrode at 600 rpm. Irregular arc wandering was found to become rapid and regular and an improvement in accuracy was reported. Myers and Brunstetter (1947) have likewise observed that an improvement in accuracy accompanies rapid rotation of the arc, and have described the use of a strong permanent horseshoe magnet for this purpose. Chandler (1949) has employed a magnet in the same manner.

A technique by which a weighed quantity of specimen is first brought into solution (either by acid attack or by fusion with an alkali carbonate or bisulphate), made up to a given volume, and then introduced dropwise in measured amount into the electrode cavity with a micro-pipette, is sometimes used in quantitative analysis. After drying, the residue in the electrode is arced. Because of its poor sensitivity, this method is not commonly employed for qualitative work.

After introduction, the solution tends to percolate into the electrode graphite or carbon and when dried it may not be suitable for arcing. It has therefore become common practice to coat the electrode surface with a waterproofing substance prior to the introduction of the sample solution. For this purpose paraffin wax, kerosene, mineral oil, and acryloid lacquer have been used. A few details of operation will be given, using paraffin wax as an example.

The wax is warmed in a suitable container and the electrode cavity dipped into the liquid; on removing the electrode the wax will dry almost immediately. The analysis solution is then pipetted out and the electrode dried in a low temperature ($\sim$80°C) oven. Because the presence of wax may interfere with the arc burn, it should be removed before arcing. This can be done quickly by holding the electrode with a pair of tongs and inserting the end opposite the loaded cavity into a Bunsen flame. The heat conducted to the cavity end is sufficient to drive off the wax completely.

It is not advisable to use a furnace for this operation, as some loss of the very volatile elements might be caused.

See also, Wilhelm (1938), Brunstetter, Myers, Wilkins, and Hein (1939), Mackenzie (1939), and Hampton and Campbell (1944).

7–3. A fundamental assumption in quantitative spectrochemical analysis. A fundamental assumption in quantitative analysis is that, under given conditions, the intensity of an emitted line within a source of excitation is directly proportional to the concentration of emitting atoms:

$$I_0 = K \cdot C,$$

or

$$\log I_0 = \log K + \log C, \tag{7–1}$$

where I_0 is the intensity of line emission and C the concentration; K is a constant.

In a quantitative analysis it is not strictly possible to measure I_0 because of the passage of emitted radiation through the absorbing outer fringe in the arc (Section 3–8). If mere traces are present, however, the factor of absorption is negligible and $I_0 = I$, where I is the intensity of the line as actually measured. A plot of log I vs log C should produce a curve of unit slope. Intensity can be measured as discussed in Chapter 8 and the concentration of the element can be made to vary by using standards, the preparation of which is described later in this chapter. If the operating conditions are kept constant, it should be possible to check the validity of Eq. (7–1).

Many plots of log I vs log C have been made and invariably the resultant curves (*working curves*) have slopes of 45°, or very near unit slope. See Hampton and Campbell (1944), Ahrens (1945b), and Marks and Hall (1946).

Sometimes working curve slopes of less than 45° are obtained; they frequently satisfy the relationship

$$I = KC^n,$$

or

$$\log I = \log K + n \log C, \tag{7–2}$$

where n is sometimes referred to as the *emission factor*, and is usually close to unity. Deviations from unit slope are usually associated either with the presence of background (Section 9–7), the presence of residual impurity of the element analyzed (Section 9–7), or with self-absorption. The factors which affect the slopes of working curves apply also to these slopes when internal standards are employed (Section 7–4).

INTERNAL STANDARDS

(Section 7–4 to Section 7–15)

7–4. General. Prior to the use of internal standards, most attempts at quantitative spectrochemical analysis had at best been semiquantitative.

Soon after Gerlach introduced his principle of internal standardization in the middle 1920's more accurate methods were developed. In lieu of measuring intensities, intensity ratios are measured, that is, the ratio of the intensity of the analysis line to that of a line of an element present in constant amount, *the internal standard*.* Such a pair of lines may be referred to as the *analysis pair*. See also Section 7–15. It must be stated at once, however, that although most accurate methods employ internal standardization it has been possible in recent years to develop procedures which avoid the internal standard but are reasonably accurate (Section 7–18).

The advantage of using an internal standard is that it affords compensation for various factors, most of them difficult to control. Some influence the intensity of line emission within the source and others disturb the accurate measurement of whatever intensity of radiation has been emitted. The first category includes all those factors which influence arc temperature. One example is a change in composition of the arc gas and the length of the arc column by wandering of the cathode spot. A variation of the arc length will also change the general intensity of radiation per unit volume. Poor control of arc wandering across the spectrograph slit, failure to time the exposure exactly, and lack of uniformity in the technique of photographic development are included in the second category. Without internal standardization it is necessary to weigh the specimen accurately. Because very small amounts usually have to be weighed and transferred to the electrode cavities, these operations may introduce errors which would be compensated in the presence of an internal standard. When internal standardization is employed it is not necessary to weigh the specimen. Approximately the same amount of each specimen should be arced, however. This is easily ensured by using electrodes of the same size and always filling the cavities to the brim.

The internal standard may be either an element present as a major constituent or an element which is added to the specimen in constant amount. For the analysis of minerals, rocks, and soils it is frequently impossible to use a major component as an internal standard because its abundance is likely to vary considerably from specimen to specimen. For more specific analyses, that is, analyses of one mineral type, it is feasible to use a major constituent as an internal standard. For example, weak zinc lines might be used as internal standard lines for the analysis of some minor elements in *sphalerite*. Another example is the analysis of iron in glass sands; here it has been possible to use weak lines of silicon as internal standard lines.

If an internal standard is used, let I_s = intensity of the internal standard

* A variable internal standard is also sometimes used (pp. 80–81).

line and I_a = intensity of the analysis line; n_s and n_a are their respective emission factors, K_s and K_a their respective constants, and C_s and C_a the respective concentrations of internal standard and analysis elements. Then,

$$\log \frac{I_a}{I_s} = \log \frac{K_a}{K_s} + \frac{n_a}{n_s} \log \frac{C_a}{C_s}. \tag{7-3}$$

By definition, C_s is constant, and Eq. (7–3) can be rewritten as

$$\log \frac{I_a}{I_s} = \log K + n_a \log C_a. \tag{7-4}$$

In spectrochemical analysis, it is common to plot log I_a/I_s vs log C_a, and this plot should produce a curve of unit slope, as in Section 7–3, if n_a = unity. Scott (1946) has made some careful observations of the slopes of curves produced from such plots and reports that in all examples the slopes are 45° or very nearly so. Some of his data are given in Table 7–1. An alumina base containing 5.0% Fe_2O_3 as internal standard element was used, and the internal standard lines were various iron lines. Several other analysts have reported working curve slopes of unity or very near unity when employing internal standards. See Hasler and Kemp (1944), Nachtrieb, Johnson, and Dress (1943), and particularly Strock (1945).

Although internal standards are usually present in constant amount, *variable internal standards* have been used. Modifications of this general procedure have been employed. Herman (1948) describes the analysis of tantalum and niobium in a two-component mixture of Ta_2O_5 and Nb_2O_5.

Table 7-1

Slope angles for working curves (corrected for background)

Element	Line	Slope
Cr	4254	44.5°
Co	3453	45.5°
Ni	3414	44.5°
Ag	3280	44.0°
V	3185	45.0°
Mo	3170	45.0°
Be	3131	45.0°
Ga	2943	45.5°
Sn	2840	45.0°
Pb	2833	45.0°

Here one component is used as the internal standard with respect to the other (see Chapter 19).

Kvalheim (1941) describes a method for analyzing vanadium in ores and slags, using iron as a variable internal standard. Iron is determined chemically, and a working curve is obtained by a plot of log I_a/I_s against log %V/%Fe. A similar but modified general procedure is described by Davidson and Mitchell (1940a) and Scott (1946) for the analysis of several elements in soils, using iron as a variable internal standard. Several working curves (log intensity ratio vs log concentration of analysis element) are prepared for various concentrations of iron. A series of parallel working curves is thus obtained, from which it is possible to construct a correction curve which permits the use of a single working curve. This curve is the one for 5.0% Fe_2O_3. The iron content must be known and may be determined colorimetrically. See Chapters 11 and 22 for other references to the use of iron as an internal standard.

Other examples of the use of variable internal standards are given by Hasler, Harvey, and Dietert (1943), Coulliette (1943), and Churchill and Russell (1945).

7–5. Choosing an internal standard. Several factors must be considered when an internal standard is to be selected. These are as follows.

Major factors.

(1) If the internal standard is to be added, it should be an element which has a negligibly small concentration in the analysis specimens.

(2) The rates at which internal standard and analysis element volatilize should be very similar.

(3) Internal standard and analysis lines should have similar excitation potentials.

(4) The internal standard line should be free from self-absorption.

(5) Analysis and internal standard lines should be roughly the same wavelength, so as to reduce errors due to the photographic measurement of radiant energy.

(6) If the internal standard is added, it should be in a very high state of purity with respect to the elements sought.

Factors usually of less importance.

(7) The element chosen as an internal standard should, if possible, be applicable to a relatively wide compositional variation, and consequently the presence of so-called "extraneous elements" should not influence the intensity ratio of the analysis pair of lines.

(8) The ionization potential of the internal standard element should be similar to that of the analysis element.

Table 7-2

Atomic number (Z)	Element	Igneous rocks g/metric ton (1 g/ton = 0.0001%)	Atomic number (Z)	Element	Igneous rocks g/metric ton (1 g/ton = 0.0001%)	Atomic number (Z)	Element	Igneous rocks g/metric ton (1g/ton = 0.0001%)	Atomic number (Z)	Element	Igneous rocks g/metric ton (1 g/ton = 0.0001%)
1	H	Present	25	Mn	1000	49	In	0.1	73	Ta	2.1
2	He	0.003	26	Fe	50000	50	Sn	40	74	W	1.5 - 69
3	Li	65	27	Co	23	51	Sb	1**	75	Re	0.001
4	Be	6	28	Ni	80	52	Te	0.0018**	76	Os	Present
5	B	3*	29	Cu	70	53	I	0.3	77	Ir	0.001
6	C	320*	30	Zn	132	54	Xe		78	Pt	0.005
7	N	46.3	31	Ga	15	55	Cs	7	79	Au	0.005
8	O	466000	32	Ge	7	56	Ba	250	80	Hg	0.077 - 0.5
9	F	600 - 900	33	As	5	57	La	18.3	81	Tl	0.3 - 3
10	Ne	0.00007	34	Se	0.09	58	Ce	46.1	82	Pb	16
11	Na	28300	35	Br	1.62	59	Pr	5.53	83	Bi	0.2
12	Mg	20900	36	Kr		60	Nd	23.9	84	Po	0.0000000003
13	Al	81300	37	Rb	310	61	Pm	Presence unsettled	85	At	Present
14	Si	277200	38	Sr	300	62	Sm	6.47	86	Rn	Present
15	P	1180	39	Y	28.1	63	Eu	1.06	87	Fa	Present
16	S	520	40	Zr	220	64	Gd	6.36	88	Ra	0.0000013
17	Cl	314	41	Cb	24	65	Tb	0.91	89	Ac	0.0000000003
18	A	0.04	42	Mo	2.5 - 15	66	Dy	4.47	90	Th	11.5
19	K	25900	43	Tc		67	Ho	1.15	91	Pa	0.0000008
20	Ca	36300	44	Ru	Present	68	Er	2.47	92	U	4
21	Sc	5	45	Rh	0.001	69	Tm	0.20	93	Np	Probably present
22	Ti	4400	46	Pd	0.010	70	Yb	2.66	94	Pu	Present
23	V	150	47	Ag	0.10	71	Lu	0.75	95	Am	Probably present
24	Cr	200	48	Cd	0.15	72	Hf	4.5	96	Cm	Probably present

* considerably higher content in sedimentary rocks
**uncertain value

(9) The atomic weight of the internal standard element should not differ much from the atomic weight of the analysis element if either is light.

*General.**

Once chosen, the concentration of the internal standard should be so adjusted that the intensity of the internal standard line lies at a level which is approximately at the middle of the range of intensities of the analysis line, or lines, used. If, for example, the analysis line is very weak and lies on the toe of the calibration curve (Section 9–1), whereas the internal standard line is far more intense, any slight inaccuracy in plotting the calibration curve would cause a large error in the measurement of the intensity ratio. If the concentration of the analysis element varies widely, several analysis and internal standard lines should, if possible, be used.

It is not always possible to fulfill all these requirements when selecting an internal standard, and a best compromise must usually be made. When such a selection is made, it is convenient to consider each factor in the order given above, which in a general way is the order of importance.

7–6. Factor No. 1: Purity of specimen with respect to internal standard. In mineral or rock analysis in particular, it is sometimes difficult to obtain an internal standard that is not likely to be present in some quantity in the analysis specimen. When the selection of such an element is attempted a general knowledge of geochemistry is helpful, and much useful information on the abundances of different elements may be obtained from V. M. Goldschmidt's publications on geochemistry and from Rankama and Sahama's book (1950), which includes modern data.

A major proportion of the earth's crust is composed of igneous rocks (primary silicate rocks). Table 7–2, which has been adapted from Rankama and Sahama's book, gives abundance data on the elements in these igneous rocks and may be used as a general reference to the abundance of the elements in the earth's crust as a whole.

For the sake of convenience most igneous rocks may be classified under two very broad groups, acid rocks and basic rocks. Table 7–3 gives abundance data on those elements which can be detected and determined spectrochemically in a rock type characteristic of each group; a granite has been taken from the acid rock group and a diabase from the basic rock group. The elements given are, with some modifications, from Ahrens (1950) and

* Internal standardization is invariably more effective when internal standard and analysis elements have the same anionic bonding; for example, both are silicates, both are sulfides, etc. A further improvement is often attainable when both are present as structure constituents of the same crystal. See for example use of potassium as internal standard for the analysis of rubidium in *lepidolite*, Section 12–2.

Table 7-3

Element	Granite %	Diabase %	Element	Granite %	Diabase %
BeO	0.001	n.d.*	CoO	0.0005	0.004
La_2O_3	0.005	n.d.*	Cr_2O_3	0.001	0.03
Y_2O_3	0.005	n.d.*	V_2O_3	0.0005	0.03
Nd_2O_3	0.005	n.d.*	Sc_2O_3	0.0005	0.005
BaO	0.2	0.02	CuO	0.001	0.01
SrO	0.05	0.10	GeO_2	0.0005?	n.d.*
Rb_2O	0.05	0.003	Tl_2O	0.0003	n.d.*
Cs_2O	0.002	n.d.*	Nb_2O_5	0.01	n.d.*
Li_2O	0.01	0.002	Ag_2O	n.d.*	0.0002?
Ga_2O_3	0.002	0.002	SnO_2	0.01	n.d.*
PbO	0.003	0.00004	B_2O_3	0.001	n.d.*
NiO	0.0005	0.005	F	0.1	0.02

*Usually not detectable

include only detectable minor elements and not such major ones as Fe, Na, Mg, Ti, Ca, and others which are, of course, easily detectable. Other elements may be detected, provided that special techniques such as the furnace procedure (Section 5–5) or a preliminary chemical concentration (Section 7–21) are employed. These elements are not included because they are not normally likely to interfere when they are used as internal standards in the common silicate rocks, and only those detectable by usual procedures have been given.

The presence of traces of these elements does not necessarily preclude their use as internal standards. Much will depend on the amount of internal standard added and what lines are used. Thus Kvalheim (1947) has used strontium as an internal standard for the analysis of several elements in rocks. Inspection of Table 7–3 shows that the abundance of strontium in common rock types is of the magnitude of 0.05–0.1%. But since Sr 2933, a weak line, was used, it did not appear at these concentrations and because a considerable amount of internal standard element had

been added, the presence of a small amount of strontium in the specimens analyzed caused no interference. (See also Dennen, 1949.)

7–7. Factor No. 2: Volatilization rates. The factor of selective volatilization is of extreme importance when using d.c. excitation of powders. Because cathode layer excitation necessitates the use of a small electrode and the specimen is made to volatilize from the cathode, selective volatilization is not so marked and is not such a critical factor as when anode excitation and larger electrodes are employed.

Criticism has been levelled at the use of the d.c. arc for quantitative analysis because of its supposedly poor reproducibility. Much of this has without doubt arisen because of the difficulty in obtaining a really suitable internal standard; a large difference in rates of volatilization is usually the major contributing cause for poor reproducibility.

Table 7-4

Reproducibility (Standard deviation)	Category
$< \pm$ 3.0%	Excellent (unusual)
$\pm$ 3.0 - 5.0%	Very good
$\pm$ 5.0 - 10.0%	Good
$\pm$ 10.0 - 20.0%	Fair
$\pm$ 20.0 - 40.0%	Poor
$> \pm$ 40%	Very poor

Where it has been possible to find an internal standard that volatilizes in a manner very similar to that of the analysis element, good reproducibility is usually reported. For convenience of discussion, an arbitrary reproducibility scale is given in Table 7–4. This scale is meant to apply only to the d.c. arc analysis of minerals, rocks, soils, and related materials.

If the internal standard volatilizes very differently from that of the analysis element, the reproducibility may be disastrously poor, and it is then wiser to dispense with its use. A question immediately arises as to how closely the manner of volatilization of the internal standard must follow that of the analysis element if the purpose of the internal standard is to improve accuracy. The answer must frequently be sought by trial, that is, by arcing a specimen a number of times and computing standard deviations with and without internal standardization. A good indication may, however, be obtained with the aid of Fig. 7–1 (a), (b), (c), (d), and (e). Each shows two selective volatilization curves, one for a line of the analysis

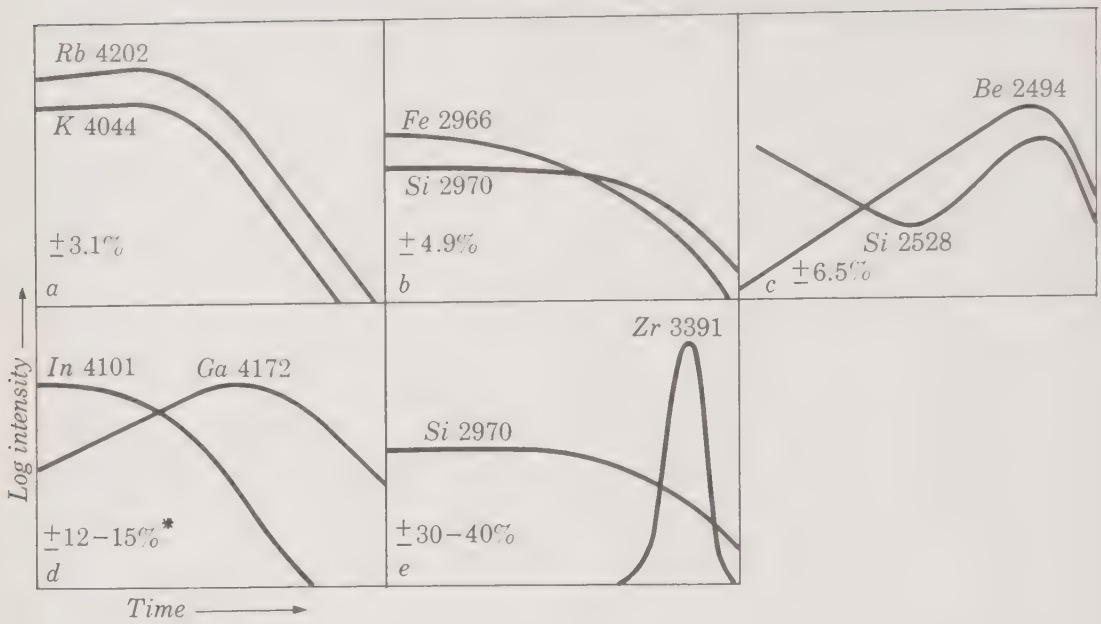

Fig. 7–1. Selective volatilization curves for several analysis element-internal standard element pairs. (a) shows ideal conditions, whereas at conditions as in (e) no attempt should be made to employ silicon as an internal standard for the analysis of zirconium in a glass sand. Standard deviations are given for each example. *The standard deviation of ±12–15% refers to a *synthetic base material* and should not be compared with the reproducibility given in Table 11–2 for the determination of gallium in rocks (±5–8%).

element and one for a line of the internal standard. In each example the other factors which influence the selection of an internal standard are considered to play a minor or negligible role. Standard deviations are given in each example, and it is readily seen that standard deviation decreases regularly with the closeness of fit of the two curves.

In examples (a), (b), and (c) in Fig. 7–1, internal standardization has provided a marked improvement in reproducibility. In (d) reproducibility is about the same with and without internal standardization, whereas in (e) it is far better to determine zirconium in a glass sand without an internal standard than to attempt the use of silicon (which, however, is a good internal standard for iron).

7–8. Factor No. 3: Excitation differences. Very little quantitative information is available on how great a difference of excitation is to be tolerated in an average analysis. It may be said that in general an arc (atom) and a spark (ion) line pair should not be used for precise work, particularly if the composition of the specimens is likely to vary. On some occasions, however, it has been possible to develop a reasonably accurate method even if an atom and ion line pair has been used. Much depends on the

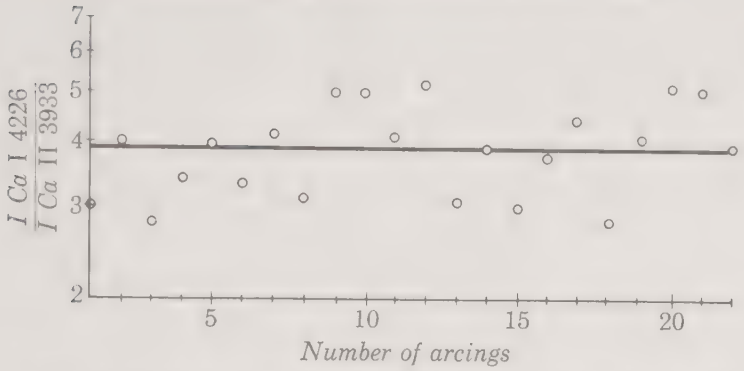

Fig. 7–2. Plot showing distribution of the ratio I Ca I 4226/I Ca II 3933 about the mean. Very erratic arc and large spread of points. Standard deviation ±30–40%

smoothness of the arc burn and some examples will be given to illustrate what is meant by such a statement.

The dried fluoride remaining after hydrofluoric acid treatment of a *mica* specimen was arced a number of times. Fig. 7–2 shows a plot of $\frac{I \text{ Ca } 4226}{I \text{ Ca } 3933}$ vs number of arcings. Operating details were as given by Ahrens (1949). Ca 4226 is a low temperature atom line (excitation potential = 2.9 volts), whereas Ca 3933 is an ion line (*total* excitation potential = 9.2 volts). The spread of points about the mean is very marked and the standard deviation is about ± 30–40%. This is a striking indication of how large an error can result from the use of an arc and a spark line. As both lines are of the *same* element, such factors as volatilization differences, inhomogeneity of specimen, etc., do not influence the line intensity ratio, and the relatively poor reproducibility is due only to excitation differences. Because the fluoride residue arcs very poorly indeed, the standard deviation of ± 30–40% is larger than that which would normally be found.

Kvalheim (1947) reports the use of Ca 3179, an ion line, for the analysis of calcium in rocks and allied materials, using an atom line of strontium as an internal standard. Anode excitation was employed and a smooth-burning arc was obtained by dilution of the specimen with carbon and the use of a small-diameter anode. The method has been applied in the Department of Geology, M. I. T., by Dennen (1949), who has found the reproducibility of the calcium determinations quite satisfactory. This would appear somewhat surprising from what has been said about the ratio $\frac{I \text{ Ca } 4226}{I \text{ Ca } 3933}$ Consequently an examination was made of the ratio of Ca 3158* to a

* Ca 3158 is an ion line which belongs to the same multiplet as Ca 3179, and hence observations on the intensity behavior of Ca 3158 refer also to Ca 3179. Measurements were made on Ca 3158 in this instance, however, because its photographic density was more suitable for microphotometric measurement.

neighboring calcium atom line, Ca 3006, by repeatedly arcing a rock specimen in accordance with the operating details given by Kvalheim. Fig. 7–3 gives a plot of $\frac{I \text{ Ca } 3006}{I \text{ Ca } 3158}$ vs number of arcings and should be compared with Fig. 7–2. The points in Fig. 7–3 have a standard deviation of ± 6.1% from the mean, whereas in Fig. 7–2 the standard deviation is ± 30–40%. In each example an atom-ion line pair has been used and the marked difference in standard deviations appears to be mainly due to a difference in the smoothness and reproducibility of the burn of the arc. Thus, whereas the time for a complete burn of specimen (using the technique for the analysis of calcium in rocks and allied materials) is invariably within ± a few seconds of sixty-five seconds, the total period of arcing for the fluoride residues varies from one to three minutes. Further, the ratio $\frac{I \text{ Ca } 4226}{I \text{ Ca } 3933}$ changes rapidly with time when a fluoride residue is arced and is 5.6 times greater at the beginning than at the end of the arcing period.

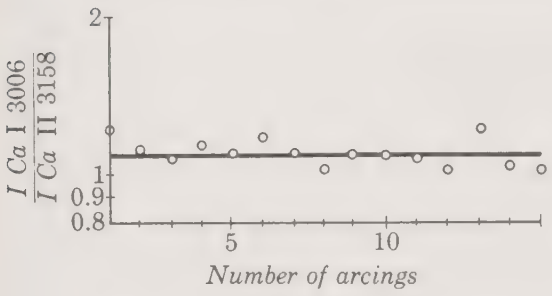

Fig. 7–3. Plot showing distribution of the ratio I Ca I 3006/I Ca II 3158 about the mean. Very smooth-burning arc and small spread of points. Standard deviation ±6%.

When a very satisfactory arc burn is obtainable, lines of a greater difference in excitation potential are tolerated and a single internal standard may often be used for the analysis of a relatively large number of elements. If the procedure employed produces a very erratic arc, the choice of an internal standard is far more critical, and usually a separate internal standard element has to be used for each element sought (or, at best, for each few elements sought). Some examples of relatively ideal analysis element-internal standard element pairs which can usually provide satisfactory reproducibility even under poor conditions of arcing are K-Rb, Pb-Bi, various pairs of rare earth elements, Ca-Sr, Sr-Ba, Sr-Ca, Zr-Hf, Ag-Cu, Fe-Co, and a few others.

One instance of the use of such a pair of elements under poor conditions of arcing is shown in Fig. 7–4, a plot of the ratio $\frac{I \text{ Rb } 4202}{I \text{ K } 4047}$ vs number of arcings of the fluoride residue of mica, to which reference has already been made. The spread of points about the mean is slight, and even under such extremely poor conditions of arcing the standard deviation is only

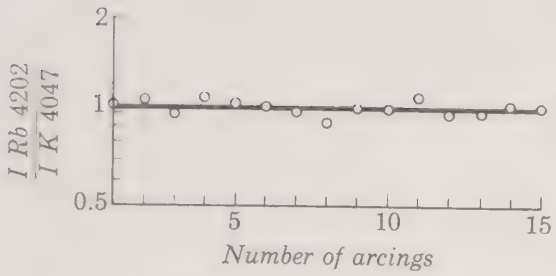

Fig. 7–4. Plot showing distribution of ratio I Rb I 4202/I K I 4047 about the mean. Very erratic arc but small spread of points. Standard deviation ±5.0%.

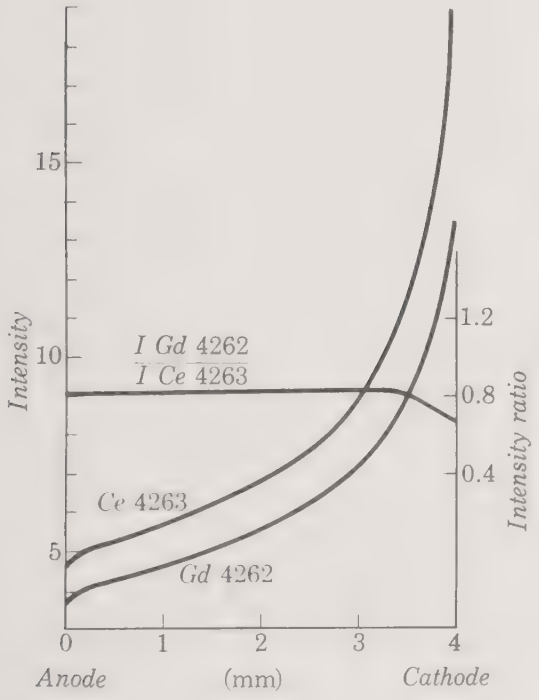

Fig. 7–5. Longitudinal distribution of intensity (Ce 4263 and Gd 4262) and intensity ratio (I Gd 4262/I Ce 4263). Because of similar excitation characteristics of the two lines, the intensity ratio remains constant along most of the arc length.

± 5.0%. It is known that rubidium and potassium volatilize very similarly and that Rb 4202 and K 4047 have very similar excitation potentials. (See also Section 23–3.)

These examples show how difficult it is to make a definite statement as to how large a difference between excitation potentials can be tolerated before quantitative reproducibility is seriously impaired. Naturally it is safer and generally more desirable to choose an internal standard line which has a similar excitation potential to that of the analysis line. So very much depends on the smoothness of the arc burn and on the amount of compositional change from specimen to specimen that it seems wisest not to adopt too rigid an attitude as to what differences in excitation potentials can be tolerated. When in doubt, the analyst should attempt the use of the line pair, note its behavior, and compute its reproducibility.

Because temperature varies longitudinally in the arc, some information on how the intensity ratio of a line pair varies at different temperatures may be obtained by determining intensity ratios at various points. To make the test more stringent there should be a relatively large longitudinal temperature variation. The use of a small amount of specimen and a very long arc are aids. Fig. 7–5 (after Fassel, 1949) shows the longitudinal intensity distribution

for Gd 4262 (the analysis line) and Ce 4263 (the internal standard line), and the intensity ratio variation of $\frac{\text{Gd } 4262}{\text{Ce } 4263}$. Because each component of the line pair has very similar excitation characteristics, the intensity distribution curves are very similar and the intensity ratio $\frac{\text{Gd } 4262}{\text{Ce } 4263}$ remains virtually constant along most of the arc column.

Consequently Ce 4263 is well suited with respect to excitation properties as an internal standard line for Gd 4262. Dennen (1949) has made several similar intensity distribution plots. A consideration of longitudinal intensity distribution for analysis and for internal standard lines becomes particularly important when cathode layer excitation is used (see Section 7–23).

Although the excitation potential of a line is a convenient measure of its energy of excitation, useful information on such energies can also be obtained by an examination of reports given on the furnace spectra of the elements. For many years A. S. King has employed a temperature-controlled furnace to excite spectra and has classified lines according to temperature. Lines which emit their highest intensities at relatively low temperatures are classified as low temperature lines, whereas those most intense at high temperature are high temperature lines. It is thus possible to classify the lines of the arc spectrum of an element into various temperature classes. Because excitation in the furnace is purely thermal and excitation in the arc is largely thermal, temperature observations on the emission of lines in the furnace may be taken as an indication of the excitation energies of lines in the arc. If the internal standard and analysis lines have the same furnace temperature classification, their excitation energies will be very similar. The observations on furnace spectra have been reported in several volumes of the Astrophysical Journal.

7–9. Factor No. 4: Self-absorption in the internal standard line. Were it not for the fact that the amount of self-absorption fluctuates considerably, the factor of self-absorption would not be so serious when present in the internal standard line. Once a concentration at which a line begins self-absorption has been reached, the ratio of the intensity of that line to the intensity of a weaker one not self-absorbed cannot be reproduced very accurately even if both lines belong to the same multiplet. If there is therefore some self-absorption in the internal standard line, its use will not provide a high accuracy even if it is otherwise an ideal line. Unfortunately, it is not easy to detect self-absorption by an inspection of the line on the plate unless it is extreme and the line shows self-reversal.

The presence of self-absorption may be ascertained as follows. If the line belongs to a multiplet for the components of which relative intensities are known, measure the ratio of the intensity of the internal standard line to that of another component line of the multiplet which is less intense, preferably by a factor of ½ or more. A decrease in this experimentally-determined ratio from the known ratio is indicative of self-absorption. If the relative intensities are not known, *decrease* the concentration of the internal standard by a factor of two or more and determine whether there is an *increase* in the value of the ratio of the intensity of the internal standard line to that of a weaker line. If there is, self-absorption is present in the internal standard line at the concentration employed. Should it be impossible to find a convenient weaker line of the same multiplet, another weaker line with roughly the same excitation potential can be used.

As an example of an attempt to ascertain the presence of self-absorption in a line, it was desired to know whether Cu 3247 showed any self-absorption at a very low concentration (0.001–0.01%) in diabase. Cu 3247 is the more intense component of the well-known doublet Cu 3247–3274. According to the sum rule, I 3247/I 3274 should equal 2.0. Several determinations of this ratio as emitted from the specimen of diabase were made, and these are given in Table 7–5. If the sum rule intensity ratio is correct, these ratios indicate that Cu 3247 is self-absorbing. Later measurements corroborated this conclusion because the ratio as emitted from a specimen of lower copper concentration approached 2.0. A further indication of the presence of self-absorption is the relatively poor reproducibility of the intensity ratios given in Table 7–5.

Table 7-5

$\frac{\text{I Cu 3247}}{\text{I Cu 3274}}$
1.25
1.34
1.32
1.13
1.36
1.32

The more exhaustive data given in Table 7–6 provide an indication of the magnitude of errors which may arise from the use of a self-absorbed line as an internal standard. Each line referred to in Table 7–6 is a component of a silicon multiplet group of which Si 2516 is the most intense. The intensity of Si 2528 > intensity of Si 2519. The latter line is considered to be free from self-absorption under these working conditions (as given for silicon in Section 23–2). Likewise, self-absorption is usually negligible for Si 2528, whereas Si 2516 shows some self-absorption. The degree of self-absorption is not high, however, and Si 2516 shows no trace of the incidence of self-reversal which only becomes apparent at much higher concentrations of silicon.

The standard deviation of ± 1.9% for $\frac{I \text{ Si } 2528}{I \text{ Si } 2519}$ is probably partly due to microphotometric error, although a self-absorption error may have contributed slightly to the total. The deviation of ± 4.6% for $\frac{I \text{ Si } 2516}{I \text{ Si } 2519}$ is due mainly to the presence of self-absorption in Si 2516. Because the lines examined belong to the multiplet of a single element, the presence of self-absorption is the only contributing source of error (other than a slight

Table 7-6

$\frac{\text{I } 2528}{\text{I } 2519}$	$\frac{\text{I } 2516}{\text{I } 2519}$
(% deviation from mean)	(% deviation from mean)
-2.0	+2.1
-3.0	+9.7
-2.0	-1.0
+1.3	-1.2
+3.0	+4.3
-1.2	+7.5
0.0	+1.0
+3.0	-0.6
-3.0	-7.5
+1.2	+4.8
-1.3	-1.0
-1.3	-6.0
+3.0	-11.0
+5.0	+3.7
0.0	+0.6
0.0	-6.5
-1.0	+5.4
Standard deviation ±1.9%	Standard deviation ±4.6%

microphotometric error). Had Si 2516 been used as an internal standard line for a given analysis, the presence of self-absorption alone would have introduced a considerable error. When the degree of self-absorption increases, reproducibility of the ratio of its intensity to that of another line becomes considerably poorer.

7–10. Factor No. 5: Separation of internal standard and analysis lines. The permissible separation of the analysis and internal standard lines depends to a considerable extent on the type of plate emulsion used. For highest accuracy the lines should preferably be of like wavelength and so closely spaced that local variations of photographic development will

influence not one but both of the lines. The properties of the photographic emulsion itself are not perfectly uniform and widely separated lines may be located in areas of slightly different emulsion properties. Despite the possibility of error from such sources, however, it is often feasible to use a line pair whose components are widely separated, provided the gamma (Section 9–2) of the plate remains constant over the wavelength range used and the very highest accuracy is not desired. Because gamma may change very rapidly over certain wavelength ranges in some emulsion types, this factor may restrict the wavelength difference of analysis and internal standard lines; much depends on the desired accuracy (see discussion in Section 9–2).

7–11. Factor No. 6: Stability of the intensity ratio of the analysis pair to compositional changes. Frequently the element sought must be analyzed in a wide variety of compositional types and a question arises as to the stability of the intensity ratio of the analysis-internal standard line pair in regard to such changes. Much time and effort will be saved if the intensity ratio is insensitive to compositional changes and only one working curve, constructed for a given base material, need be used. Otherwise several working curves must be drawn, one for each compositional type. In Chapter 8 the influence of compositional changes on line intensity is discussed and the conclusion is drawn that more frequently than not compositional changes do affect line intensity. Nevertheless, it is sometimes possible to use a given internal standard for the analysis of an element in a wide variety of specimen types without having to prepare several working curves for each separate base material. Thus Kvalheim (1941) found that whereas the use of iron as an internal standard was not satisfactory for the analysis of vanadium in a variety of specimen types (Section 22–2), chromium satisfied this need and the intensity ratio of the chromium-vanadium line pair was not disturbed by compositional variations. Analysis pairs from the ideal analysis element-internal standard element pairs (Section 7–8) are quite often stable over a considerable variation in composition.

7–12. Factor No. 7: Ionization potential differences. When the arc temperature changes, the degree of ionization of any element varies in accordance with Saha's relationship (Section 3–3). If, for example, the internal standard element has a low ionization potential, whereas that of the analysis element is high, a change in source temperature will alter the degree of ionization for both elements in the same direction but not to the same extent. The ratio $\left\{ \dfrac{\text{atoms (or ions) of analysis element}}{\text{atoms (or ions) of internal standard element}} \right\}$ is then

not constant, and the intensity ratio of the analysis pair will change even if the excitation potential of each component line is the same.

7–13. Factor No. 8: Atomic weight differences. As the rate of diffusion of an element upwards in the arc column is in part dependent on its mass, elements of varying mass will move with different speeds. For a pair of elements such a factor is not likely to be important unless one of the elements comprising the analysis pair is a light one and the other a heavy one. Thus, although lithium and cesium have very similar spectral characteristics in the arc, the difference in atomic weight is large, and *ideal* internal standardization of one for the other is not expected. Unfortunately, experimental data on the effects of atomic weight differences on reproducibility are lacking.

7–14. Factor No. 9: Purity of the internal standard. Unless a very pure salt of the internal standard to be added is available, it is likely to contain disturbing traces of the analysis element if both elements belong to the same periodic group. For example, calcium is a likely internal standard for

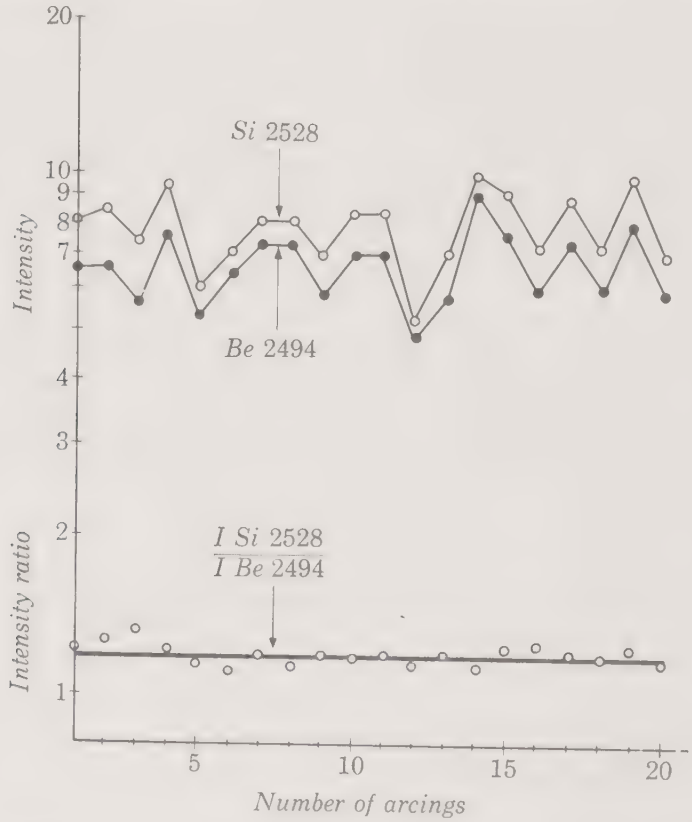

Fig. 7–6. These plots illustrate the efficacy of Be 2494 as an internal standard line for Si 2528, using the operating conditions outlined in Section 23–2.

the analysis of strontium and barium, but even most so-called high-grade calcium salts contain appreciable traces of strontium and less amounts of barium, and must therefore be purified before use. Very pure oxides and salts of most elements are procurable from Johnson Mathey, Ltd., London, and can often be added without further purification.

After each factor has been considered and investigated, the efficacy of the selected internal standard must be examined. A number of arcings are made of one or more specimens. A convenient method of showing the behavior of the internal standard is to draw two plots, one (a) of the log intensity of the analysis line vs each arcing, and another (b) for the internal standard line. From these two plots it is possible to observe clearly how satisfactory is the compensation afforded by the internal standard. Finally, the plots in (a) and (b) can be combined, and a plot made of the analysis line pair log intensity ratio vs each arcing. Fig. 7–6 (after measurements by Mrs. L. G. Gorfinkle in the Cabot Spectrographic Laboratory, M. I. T.) shows such plots. Si 2528 is the analysis line and Be 2494 the internal standard line; operating conditions are as outlined in Section 23–2. In this example, the internal standard has compensated satisfactorily and its use improves the reproducibility of the silicon determination considerably.

As a postscript to this discussion on the choice of internal standards, it should be stressed that the final proof of the efficacy of an internal standard must be sought by trial. Theory can only indicate and act as a guide. Even if several of the conditions for satisfactory internal standardization are apparently violated, a satisfactory reproducibility may nevertheless be attainable provided the arc behaves ideally.

7–15. Homologous pairs. When internal standardization was first attempted, Gerlach and Schweitzer introduced the use of the so-called *homologous line pairs* for quantitative analysis. These are actually analysis pairs (analysis line-internal standard line) but fulfill an additional requirement, namely, equality of intensity. From a series of standards intensity equality is determined for several homologous line pairs, which can then be used for the quantitative analysis of unknowns. Homologous line pairs are not in very common use nowadays in this narrower sense. Their use does, however, provide some advantages. A null method of photometry is furnished and because the component lines of a homologous pair are equally dense, the effect of a heavy background as a possible source of error is removed (Section 9–7). Some spectrochemists retain the term "homologous pairs" in place of "analysis pairs."

7–16. The presence of self-absorption in the analysis line. Just as it is desirable to have an internal standard line free from self-absorption, the

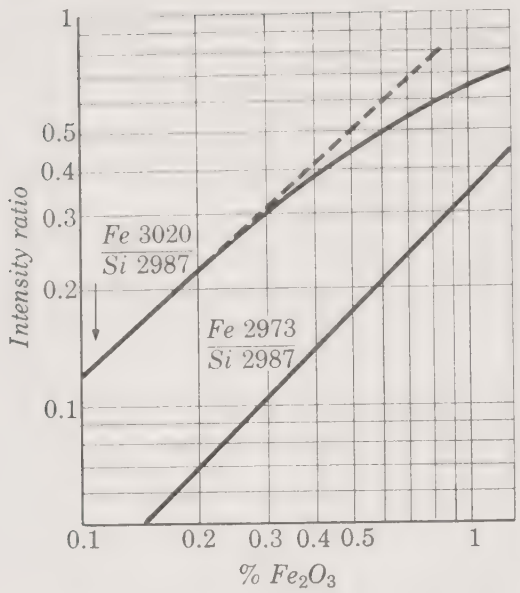

Fig. 7–7. Two working curves for the analysis of iron in glass sand. Self-absorption begins in Fe 3020 before it starts in Fe 2973 because although the low levels for both lines are the same, Fe 3020 is considerably more intense. The concentration at which self-absorption begins is indicated by the deviation from linearity. The arrow marks the beginning of the *critical* concentration range.

analysis line should also be free from this disturbing factor. As self-absorption appears at relatively high concentrations, the upper limit of the range of concentrations for which a given analysis line can be employed is frequently set by the concentration at which self-absorption begins.

Methods of detecting the presence of self-absorption have already been discussed (Section 7–9). Usually a deviation from nonlinearity in the log I ratio vs log C relationship indicates the concentration at which self-absorption begins. Fig. 7–7 shows two typical working curves (see Section 9–4) as used for the analysis of iron in glass sand (Ahrens, 1944). Fe 3020 is a ground state line (excitation potential = 4.09 volts), whereas Fe 2973 (excitation potential = 4.2 volts), also a low level line whose low level is a little less than 0.1 volt above ground, is considerably less intense. The working curve slope for Fe 3020 increasingly deviates from linearity as concentration increases. At a concentration of about 0.25% Fe_2O_3, self-absorption is apparent, and above this concentration the use of Fe 3020 should be discontinued and Fe 2973 used in its stead.

For accurate quantitative work it is actually safer to discard a line showing self-absorption at concentrations considerably below the concentration at which self-absorption appears to begin. In this example the use of Fe 3020 should be stopped at about 0.1% Fe_2O_3, that is, ½–⅓ of the concentration at onset of self-absorption. This is due to the fact that self-absorption sometimes occurs within this *critical* concentration range (see Fig. 7–7). Thus a slight current of air might throw a greater proportion of the outer absorbing cloud in the direction of the light path for a time and thereby cause some self-absorption in the critical concentration range. On a few occasions the author has observed some unusually large errors within this range. These are considered attributable to self-absorption.

Strock (1936a) investigated the geochemistry of lithium, using Li 6707 and Li 6103 for its quantitative determination. Strontium was the internal

standard element. Fig. 7–8 shows some working curves as prepared from his data. Li 6707 is the lithium resonance line and is quick to show the onset of self-absorption, which is apparent at about 0.009% Li_2O. Li 6103, which is not a ground state line (low level 1.84 volts) and which is less intense, shows no self-absorption until a concentration of about 0.8% Li_2O is reached. Strock employed cathode layer excitation and the usual small diameter cathode layer electrode. He used several cathode depths and found that the concentration at onset of self-absorption could be altered markedly by changing depth. Fig. 7–8 shows that self-absorption starts at concentrations of Li_2O of 0.009%, 0.025%, and 0.09%, at cathode depths of 7 mm, 3 mm, and 1 mm, respectively.

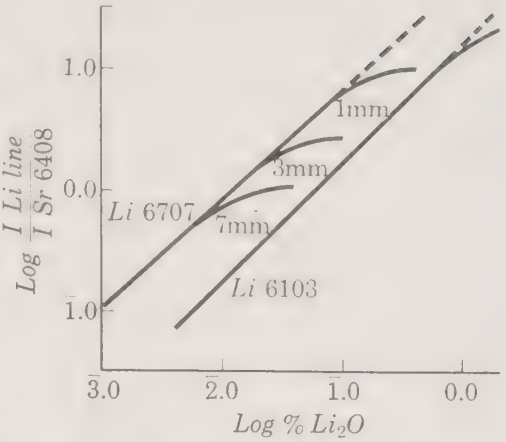

Fig. 7–8. Self-absorption is seen to begin at very low concentrations in Li 6707, which is an intense ground state line. The concentration at which self-absorption begins may be increased by using shallower electrodes.

The concentration at which self-absorption begins may be increased as shown above, or depth may be kept constant and a decrease in electrode diameter attempted. If the specimen is made to volatilize over a longer period of time, self-absorption is decreased. In this respect a graphite electrode is usually better than the hotter carbon electrode because of a quicker release of material from the latter. Arcing time for cathode excitation is usually much longer than for anode excitation, and therefore

Table 7-7

% radiation transmitted = $I/I_0 \times 100$

Relative intensity of line (arbitrary units)	25	200	400	800
With fan directing cloud toward slit	50%	40%	23%	12.5%
Without fan	87%	80%	50%	42%

a decrease in self-absorption is to be expected. The degree of self-absorption may be lowered by the use of a relatively low amperage. Dieke and Crosswhite (1943) observed that if a fan is placed in front of the source and thereby directs most of the absorbing cloud away from the light path,

the amount of self-absorption is decreased greatly. If the fan is placed behind the source, self-absorption is enhanced. Although these authors examined radiation from an iron arc, their observations apply to other arcs as well. Some self-absorption data calculated from their graphs are given in Table 7–7. These data apply to the a^5F lines of the iron spectrum.

The introduction of a fan markedly increases the amount of self-absorption in each line. As is to be expected from Section 3–8, self-absorption increases with an increase in the intensity of the line. On occasion it is possible to select regions along the length of the arc column where self-absorption is nonexistent (see observations on Fe arc in Section 3–8). This is illustrated in Fig. 7–9, which shows plots of intensities of Si 2516 and Si 2528 along the length of the arc column, using cathode excitation of a rock as described by Kvalheim (1947). Si 2516 is the more intense line and, as both lines have about the same low level, this line will be the first to show self-absorption. The general intensity of emission is greatest near the cathode and there Si 2516 shows self-absorption, as indicated by the decrease in the ratio $\frac{I \text{ Si } 2516}{I \text{ Si } 2528}$. In the region one-third of the way along the length of the arc column above the anode, Si 2516 is free from self-absorption and the ratio $\frac{\text{Si } 2516}{\text{Si } 2528}$ remains $= \sim 1.9$.

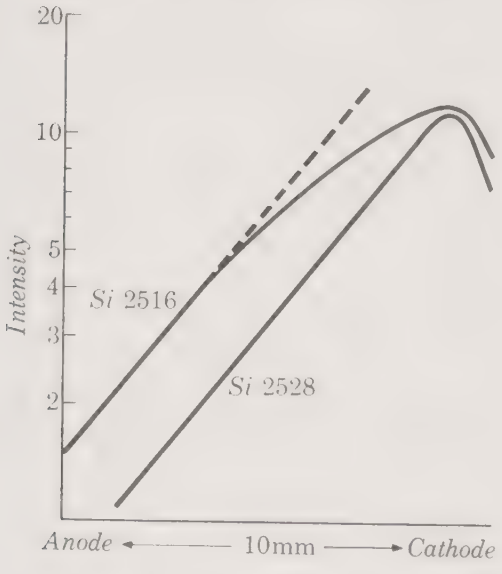

Fig. 7–9. Longitudinal intensity distribution of Si 2516 and Si 2528 (cathode excitation). Although Si 2516 shows self-absorption near the cathode, this line is free from self-absorption near the anode.

7–17. The possibility of using absorption intensity ratios in quantitative analysis. Consider a given multiplet of an element. If the concentration of the element is made to increase, a concentration will be reached at which the most intense component line of the multiplet will begin to self-absorb. For further increases of concentration, the ratio of this line to that of a weaker line of the multiplet will then change with concentration, and this ratio is therefore a function of concentration. On this basis W. H. Dennen of the Cabot Spectrographic Laboratory, M.I.T., has suggested the possibility of developing a quantitative method based on absorption intensity ratios. It is understood, of course, that be-

cause of the rather random behavior of self-absorption at any given concentration no very great accuracy could be expected. Because on a relative scale self-absorption begins at higher concentrations, the method would not apply to trace amounts. Some observations have been made on a few doublets, the relative intensities of the components of which are known. F. C. Canney of the Cabot Spectrographic Laboratory, M. I. T., has measured the intensity ratio of $\frac{\text{K } 4044}{\text{K } 4047}$ in feldspars. Fig. 7–10 shows a plot of $\frac{I\ 4044}{I\ 4047}$ vs the concentration of potassium. The intensity ratio is 2.0 at concentrations $< 0.7\%$ K_2O where there is no self-absorption by K 4044, the stronger line. Using this curve, it has been possible to make determinations of potassium in feldspar with a standard deviation of about $\pm$ 10%.

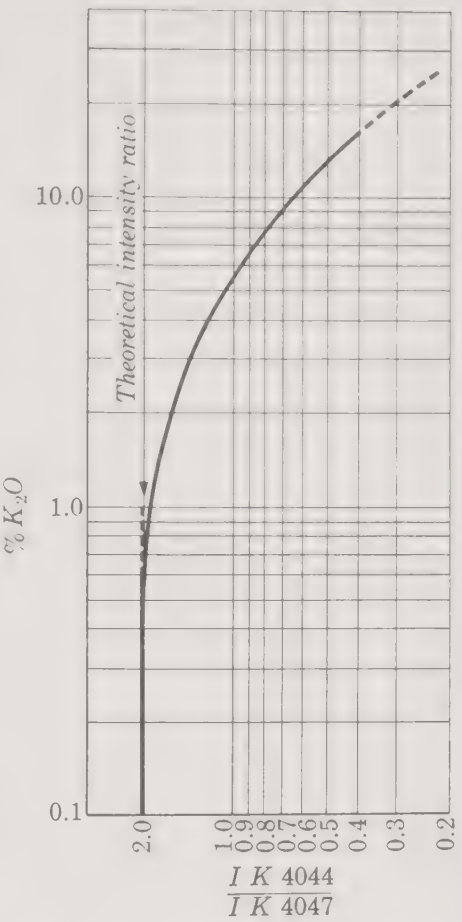

Fig. 7–10. Above $\sim$0.7% K_2O, the intensity ratio K 4044/K4047 decreases sharply with increase in the concentration of potash. Where no self-absorption is present, the ratio I K 4044/I K 4047 = 2.0, and thus obeys the sum rule (Section 2–12) exactly.

The shapes of these working curves are very sensitive to alterations of spectrograph and microphotometer slit widths.

Ease of manipulation is one special advantage of the absorption intensity ratio method. No time is spent in attempting to find a suitable internal standard. However, it does not seem probable that very accurate methods of this type will be developed unless it is possible to control the behavior of the absorbing cloud. Myers (1949) has made the suggestion that better control of the arc column for this purpose may be attained by rapidly rotating the arc with a magnet (Section 7–2).

The method outlined here is similar to that discussed by Roach and Rollins (1947) who, however, did not employ lines of the same multiplet. The use of intensity ratios of multiplet components reduces to zero possible

errors due to excitation potential differences. The accuracy of the method then depends largely on the accuracy with which the behavior of the absorbing cloud can be controlled.

7–18. Quantitative spectrochemical analysis without the use of an internal standard. For purposes of semiquantitative analysis internal standardization is rarely employed, and visual determinations of line response are usually made (Section 9–6). As mentioned in Section 7–4, however, it is sometimes possible to analyze accurately without the use of an internal standard. Source control is vital and proper quantitative accuracy is not attainable unless the arc burns very smoothly. Slavin (1938) and Leme (1938) were the first to discuss critically accurate quantitative analysis without internal standardization. These authors stress arcing the sample to completion and thus recording the total intensity of emission. For this reason this procedure is sometimes referred to as the "total energy" method. It is necessary to weigh each specimen accurately and carefully transfer the weighed sample to the electrode cavity without loss of sample. After the total intensity of emission has been recorded for unknowns and standards, a carefully controlled reference source of energy is recorded on each plate. A mercury vapor lamp or a Pfund type of iron arc (Slavin, 1940a) has been used; Hampton and Campbell (1944) use Co_2O_3 in place of Fe_2O_3 for obtaining a very reproducible reference energy source. The reference source is recorded stepwise so as to obtain a calibration curve (Section 9–1) from which the relative photographic response values of the analysis lines are converted to "iron" or "cobalt" units. A working curve (log concentration vs log "Fe" or "Co" units) is obtained by means of which the unknowns are determined.

An example of an accurate quantitative method without the use of an internal standard is given by Slavin (1941) for the analysis of iron in glass sands. Marks and coworkers have employed this general method extensively in the analysis of ores. Their method is discussed in Chapter 11 and some reproducibility data are given there. See also Barbosa and Barbosa (1945).

Although it is common practice to arc the specimen to completion, cutoff procedures have sometimes been used for the analysis of such relatively volatile elements as Li, Tl, Rb, Pb, Sn, and In in mica and feldspar. See Ahrens (1945 b) and Ahrens and Liebenberg (1950). Such a cutoff procedure cannot be applied to involatile elements, and even for volatile elements the composition of the specimens should not show a great variation.

7–19. Quantitative analysis using line width. The use of line widths as a measure of the concentration of an element was suggested simultaneously by Eisenlohr and Alexy (1937) and by Gerlach and Rollwagen (1937).

Internal standardization is employed and, in the method described by Eisenlohr and Alexy, the ratio of the line width of the internal standard line to that of the analysis line is measured. In the method employed by Gerlach and Rollwagen (which has been adopted by Coheur, 1946), the line width of one component of the analysis pair is measured at a photographic response-value equivalent to the maximum of the other. The photographic response is measured on a recording microphotometer and line profiles are obtained. Coheur measured the width of the internal standard line at a galvanometer reading equivalent to the densest portion of the analysis line and plotted this width vs log concentration as a working curve. Fig. 7–11 shows some line profiles which illustrate the method of determining line width: (a) is the profile of the analysis line and (b) the internal standard line; in (1) there is a higher concentration of the analysis element than in (2). Eastmond and Williams (1948) reversed the scheme of measurements made by Coheur, and measured the width of the analysis line at a deflection equivalent to the darkest point on the profile of the internal standard line.

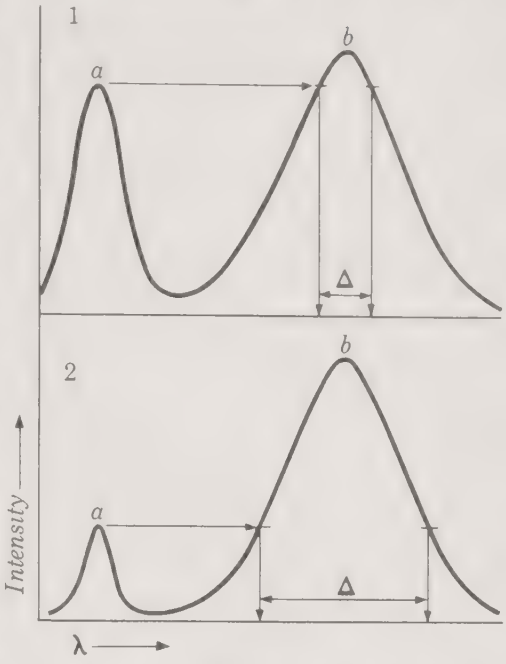

Fig. 7–11. Determination of "intensity ratios," using the method of linewidths. Δ takes the place of the usual intensity ratio as a function of the concentration of the analysis element.

Whereas ordinary methods frequently cannot be employed at relatively high concentrations because of self-absorption, the line width method is not thus affected and may therefore be used in the presence of self-absorption. The line width method is independent of exposure duration and of the conditions of development, not only within the straight line portion of the characteristic curve (Section 9–2) but also in "underexposed" and "overexposed" regions. Better results can apparently be obtained when a very large dispersion is used.

Although the line width method has not been applied to the analysis of minerals, rocks, soils, and related materials, it could undoubtedly be used for this purpose.

7–20. Preparation of standards. The standards used for the construction of a working curve should approximate as closely as possible the

chemical composition and physical characteristics of the unknowns. Ideally, the standards should be accurately chemically analyzed, naturally occurring specimens. In a few instances it has been possible to use very accurately analyzed natural specimens. For the analysis of potassium in *plagioclase* feldspars (Section 23–3), mixtures of a potash feldspar and a soda feldspar, obtainable from the National Bureau of Standards, were employed. For the analysis of iron in glass sands, Ahrens (1944) used a sand specimen from the National Bureau of Standards containing 0.072% Fe_2O_3, and an impure sand containing 1.0% Fe_2O_3. If a working curve prepared from the analyzed sand standards is compared with one obtained from standards from precipitated SiO_2 and precipitated Fe_2O_3, two parallel working curves result. These, however, are displaced by about 15%. This difference is due only to a difference in physical characteristics of the two sets of standards and illustrates a type of error which is omnipresent in spectrochemical analysis when synthetic standards have to be used.

Chemically analyzed rocks and other materials were used by Kvalheim (1947) as standards for the analysis of their major constituents. The same author (1941) employed chemically analyzed ore and slag as standards for the analysis of vanadium.

Although it is quite frequently possible to use chemically analyzed minerals, rocks, and soils for the analysis of elements present in relatively high concentrations, standards for the analysis of traces usually must be synthesized, at least in part.

Sometimes it is possible to use a specimen of the mineral type to be analyzed as base material, provided these specimens are free from the presence of the element or elements sought. If a very slight trace is apparent, the specimen may still be used, provided a correction is made for residual impurity (Section 9–7). Oftedal (1941) investigated the abundance of several minor constituents in *sphalerite* (*zinc blende*). He first employed precipitated ZnS as a base but encountered some difficulty in obtaining a smooth burn. One of several *sphalerite* specimens which had been examined qualitatively was found unusually pure, and could therefore be used as a base material. Ahrens and Liebenberg (1950) analyzed for tin and indium in *mica*, and were able to find a few specimens which were free from detectable amounts of these two elements and could therefore be used as base material. To these were added known amounts of *cassiterite* for tin, and In_2O_3 for indium.

Bray (1942) has used *feldspar*, *mica*, and *quartz* bases. In common with the observations of several other spectrochemists, the poorest sensitivity for the elements examined was found in the *quartz* matrix. Working curves in each base material were displaced considerably with respect to the others, which was only to be expected in the light of the discussion of the influence of compositional change on line intensity in Chapter 8.

If a synthetic *base* material has to be used, the analysis element can sometimes be added in the form of a naturally occurring mineral, as has been done by Strock (1936a), who added *kunzite* (for lithium) to a base made from SiO_2 + NaCl.

In many instances it is necessary to synthesize the standards completely (base material and added compound). Some analysts recommend partial sintering of these standards prior to arcing. Usually the arc burn of the sintered material is much smoother; particularly in silicate bases.

For specific mineral types, a chemical compound of approximately equivalent composition is usually used, for example precipitated ZnS and PbS for the analysis of minor elements in *sphalerite* and *galena* respectively. For the common rock-forming minerals and rock types, most of which are complex silicates, at least two or three ingredients are employed for the preparation of the base material. These ingredients are usually a salt of an alkali metal, for example Na_2CO_3, plus SiO_2 (as quartz), and Al_2O_3. CaO, MgO, and Fe_2O_3 are quite often added. An example of a simple silicate base suitable for the analysis of silicates is Na_2CO_3 (15%), Al_2O_3 (30%), and SiO_2 (55%). The mixture should be sintered prior to arcing, otherwise the arc burn will be poor. For this purpose a muffle furnace is convenient and a sinter at 1000°C for 12 hours suffices. Kvalheim and Strock (1939) employed a relatively complex base (40% *microperthite feldspar*, 16% CaO, 20% SiO_2, 18% MgO and 6% Fe_2O_3) for an investigation on the abundance of scandium in *pyroxenite*. The composition of the base is similar to that of *pyroxenite*. Because only scandium was sought, and since scandium was not present in any of the base ingredients, a complex base could be employed. However, it is often unwise to use such a base because complexity increases danger of contamination. The base used by Kvalheim and Strock would be unsuitable, for example, for the analysis of the rare element gallium because gallium is an omnipresent constituent of *feldspar*. Strock (1936b, pp. 49–53) has compiled a list of base materials that have been used by several analysts. Other examples of bases are found in Part II of this book.

SiO_2 as *quartz* is one of the most common major ingredients of a synthetic base. The reduction of large crystals of quartz to a fine powder is a tedious operation, but much effort and time can be saved if the crystals are first quite strongly heated and then chilled in cold water. They are then friable and much more amenable to grinding in an agate mortar. The use of a steel percussion mortar is then unnecessary.

The utmost care must be exercised to ensure the greatest possible purity of the base ingredients. Mitchell (1948, pp. 128–130) describes methods for the purification of Na_2CO_3, SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO, K_2SO_4, and TiO_2.

Once a satisfactory base mixture has been selected, the oxides and

sometimes the salts of the analysis elements are incorporated into it in known concentrations. A convenient dilution factor is $\sqrt{0.1}$. The compounds of the elements sought are weighed and the ratios of their weights to that of the base are adjusted to give an initial standard which contains 10%, 1%, or 0.1% of each of the elements sought, depending on the upper limit of the concentration range desired. $\sqrt{0.1}$ gm (0.316 gm) of this standard is diluted with $1.0 - \sqrt{0.1}$ gm = 0.684 gm of the base to give the second standard. $\sqrt{0.1}$ gm of this second standard is mixed with 0.684 gm of base to give the third standard. This operation is continued until the lower limit of concentrations to be analyzed is reached. Such standards will dilute as follows: 1.0%, 0.316%, 0.1%, 0.0316%, 0.01%, 0.00316%. . . . A factor of $\sqrt{0.1}$, for example ½ or 2.0, can be used, if respectively smaller or larger quantities of standard are required. Mixing is carried out in an agate mortar as already described in Section 5–1. For the use of single standards and also the so-called addition method, see Section 9–4.

If some of the elements sought show a very high sensitivity (limit of detection 0.0001%), it is wiser to use one mortar for the preparation of the first standards (0.01% and more) and another for the preparation of standards of lower concentrations. This is due to the difficulty of removing residual traces of material from the agate surface, even after grinding with quartz powder and treatment with hot mineral acids. Worn agates are the worst culprits in this respect, and once the surface is rough it is advisable to have it repolished.

Some elements which have shown their presence as residual impurities on agate mortar surfaces are lithium, thallium, and indium. Due to this residual surface impurity effect, the relative intensities of the lines do not weaken sufficiently at very low concentrations (for example, 0.0001–0.00001%), although they will do so if a fresh agate mortar is employed.

Table 7-8

Specimen type	% Nb_2O_5
Olivine gabbro	0.000008
Bytownite gabbro	0.00009
Gabbro	0.0007
Gabbro	0.0002
Hornblende bytownite gabbro	<0.000001
Hornblende gabbro	0.0001
"Merensky Reef" (Transvaal)	0.000006

7–21. Chemical concentration of elements prior to their analysis. It may be desirable and sometimes absolutely necessary to concentrate an element chemically before attempting its quantitative spectrochemical analysis. The need for some chemical concentration becomes desirable when a wide variety of specimen types are to

be analyzed. Possible deleterious effects of compositional variation (Chapter 8) on line intensities may be nullified by concentrating all elements sought in a precipitate of constant general composition. See for example discussion on the analysis of Co, Ni, Mo, Cr, V, Be, Ge, Sn, Pb, Ti, Zn and Cd in soil extracts and other materials, by Mitchell (1948, Chapter 11).

The need for chemical concentration becomes absolute when the elements sought are in concentrations below their spectrochemical detection limits. Thus Rankama (1948) was able to investigate the geochemistry of niobium exhaustively in a wide variety of rocks and minerals in most of which the niobium concentration was far below the detection limit of direct spectrochemical methods. Table 7–8 gives some actual analyses of niobium at low concentrations in basic rocks. This serves to indicate the sensitivity of the combined chemical enrichment-spectrochemical analysis procedure for the analysis of niobium. Without enrichment, the spectrochemical detection limit is about 0.01%.

Only two examples have been cited on the use of combined chemical enrichment-spectrochemical analysis methods. Such procedures have been widely employed and many examples are given in most chapters in Part II of this book. The reader should also consult Mitchell (1948, Chapter 11) for a discussion on enrichment procedures and as a source of references. *The scope of these combined procedures is immense.*

7–22. Statistical presentation of the reproducibility (precision) and accuracy of a method. Once a spectrochemical method has been developed, a reasonably accurate statement of its *reproducibility* (*precision*) and *accuracy* should be made. Most spectrochemists do provide some such information in their publications. Sometimes a clear statement of reproducibility and accuracy is given but quite frequently phrases such as "the accuracy of the method is about ± 5%" are used. Such loose statements convey little and no two readers will reach the same conclusion as to what is meant. If the method that has been developed is only semiquantitative a relatively approximate indication of reproducibility and accuracy usually suffices.

Some analysts give a determination in duplicate or triplicate and conclude that if the agreement appears reasonably good the reproducibility of the method is good. Chance can, however, play us insidious tricks and statistically such conclusions are flimsy. Because of the tedium of some chemical operations, analysts who employ wet chemical methods are often unable to make many replicate analyses and for them it might be difficult to provide reproducibility data accurately. As a result of the speed of spectrochemical analysis, however, spectrochemists cannot easily be

excused from giving indefinite information about a method that they describe as really quantitative.

As the name implies, reproducibility is a measure of the ability of a method to reproduce a determination. Precision is a synonymous term. It is expressed as a deviation from the mean of many replicate determinations. If a method is described as highly reproducible that does not necessarily mean that it is accurate. There may be a systematic error (bias) inherent in the method and the term accuracy takes into account both systematic error and reproducibility.

The frequent use of synthetic standards in spectrochemical analysis is a common source for systematic errors, because standards and unknowns are not identical. (See Chapter 8 for discussion on the effect of compositional change on line intensity.) This systematic error may be negligible or very marked. If it is negligible, or if naturally occurring standards that

Table 7-9

Analysis No.	% Fe_2O_3	% Deviation	$\left(\frac{\%}{\text{Deviation}}\right)^2$
1	0.073	+1.4	1.9
2	0.072	0.0	0.0
3	0.070	-2.8	7.8
4	0.070	-2.8	7.8
5	0.076	+5.6	31.3
6	0.068	-5.6	31.3
7	0.074	+2.8	7.8
8	0.071	-1.4	1.9
9	0.069	-4.2	17.6
10	0.075	+4.2	17.6
11	0.068	-5.6	31.3
12	0.070	-2.8	7.8
Average	0.071		
Average deviation ± 3.3%			
Standard deviation ± 4.0%			

have been accurately analyzed chemically are available, the reproducibility of the method may then be regarded as equivalent to accuracy. For a method to be accurate it must of course be reproducible. Frequently it is impossible to make a statement on the accuracy of a method because of the difficulty in checking the spectrochemical determinations. It is always possible, however, to provide information on the reproducibility of a method, for which purpose a series of replicate analyses are made.

Consider the replicate analyses of iron (as Fe_2O_3) in a glass sand (Ahrens, 1944). These are given in Table 7–9.

The mean value of 0.071% Fe_2O_3 is very slightly less than the chemical determination which is 0.072%. Because this specimen is a standard from the National Bureau of Standards, the chemical value of 0.072% is considered correct. As naturally occurring sands had been used as standards for this analysis, the slight difference between the spectrochemical mean and the chemical result are not considered significant and reproducibility may be regarded as equivalent to accuracy. In Table 7–9 the deviation (d) of each determination from 0.072% is given percentagewise; the percentage deviation squared for each determination is also given.

If the individual deviations are totalled (regardless of sign) and divided by the number of determinations (12) a value of ± 3.3% is obtained, which is one measure of the reproducibility of the method. This is the *average deviation*, which is simple to calculate and is sometimes used, but which is now largely replaced by *standard deviation* (*s*). This is a more definite measure of reproducibility. For its calculation, the squared deviations are summated; then

$$s = \pm \sqrt{\frac{\Sigma d^2}{n - 1}},$$

where *n* is the number of determinations, which in this example is 12. The reproducibility of this method, expressed percentagewise as standard deviation, is ± 4%. This means that 67% of all determinations should fall within ± 4% of the mean value. 95% of all determinations will fall within two standard deviations (± 8%) of the mean. *Probable deviation* is also sometimes used as a measure of reproducibility and is equivalent to 0.67 × standard deviation. In this example the probable deviation is ± 2.9% which means that one-half of all determinations should fall within ± 2.9% of the mean. *Average deviation* = 0.80 × standard deviation. Although a standard deviation of ±4.0% was obtained for this one specimen, Ahrens (1944) found the standard deviation to be ±4.9% when all specimens were taken into account.

Actually, for an accurate calculation of deviation, the number of replicate determinations should be far greater than 12; statisticians are usually satisfied with 30–40. However, the use of 10–12 determinations provides a reasonably accurate value for the standard deviation which for mineral, rock and soil analysis would suffice for most purposes.

In attempting to improve the precision of a determination of an unknown the analyst might make several measurements and use a mean value. In so doing the deviation will be lowered as the square root of the ratio of the number of measurements. Thus, in the above example, the standard deviation for a single measurement is ±4%. For two measurements, the

standard deviation is, $\sqrt{1/2} \times \pm 4\%$, $= \pm 2.8\%$; for three measurements $= \sqrt{1/3} \times \pm 4\%$, $= \pm 2.3\%$, and so on.

In practice, the use of triplicate measurements is convenient in attempting to improve precision. The extra time is not excessive and the deviation is lowered by almost a half. It requires an analysis made in quadruplicate to lower the deviation for a single measurement to exactly half.

For further reading on statistical evaluation of analytical data see Churchill and Churchill (1945) and Kolthoff and Sandell (1945).

7–23. Slit illumination for quantitative analysis. For the accurate microphotometric measurement of line intensity each line should be uniformly dense along the whole of its length on the plate. A system of illumination should therefore be used which provides even illumination of the slit of the spectrograph.

If cathode layer excitation is employed (Section 5–6), radiation from the desired region adjoining the cathode must first be isolated. This may be done by using a spherical condenser of short focal length which is focused on a screen and by means of which all radiation except that which is required for analysis is masked off. The transmitted segment of radiation is intercepted in front of the slit by a long focus condenser which brings it into focus at the collimator. See Strock (1936b) for further details of this method for obtaining uniform illumination. Alternatively, a single long focus lens may be used at the slit. Masking is done at the collimator (Mitchell, 1948, p. 86). Bray (1942) used a system involving the use of two cylindrical lenses.

For anode excitation any of the six methods referred to in Section 9–3 may be used. If a particular segment of the arc is to be used, the same methods as employed for cathode layer excitation are applicable.

When anode excitation is used the longitudinal intensity distribution may be nearly uniform for most lines (excluding ion lines) along almost the whole of the arc length, except near the poles.

To investigate such longitudinal intensity variations a short focus spherical condenser is employed. This single lens illumination is commonly used in qualitative analysis (Section 5–9) but has never been recommended for quantitative analysis because, by imaging the arc on the slit, possible longitudinal intensity changes are revealed on the spectrogram. However, because of the relatively uniform longitudinal intensity distribution when using anode excitation, a short focus spherical condenser appears feasible. Using anode excitation, the author has quite frequently employed a short focus lens and has obtained standard deviations of ±3–6%. Dennen (1949) employed this method of illumination for the analysis of the major constituent elements Al, Fe, Mg, Ca, and Mn in rocks and reported a very

satisfactory accuracy. Likewise, a single short focus condenser was used for the analysis of potassium, with rubidium as an internal standard (Section 23–3); the standard deviation is ±3.1%. Because of their relatively sharp longitudinal intensity changes, ion lines should not be used if high accuracy is desired when using a short focus lens.

It may be assumed therefore that notwithstanding many statements to the contrary, a spherical condenser of short focal length can be employed for accurate quantitative analysis, provided *anode* excitation is used, only *atom* lines are employed, and a relatively small segment length of the total arc length is used. The use of this simple lens system for both qualitative and quantitative analysis offers the advantage of convenience.

Although the longitudinal intensity changes may be comparatively slight, the short focus spherical condenser is not suitable when a large segment length of the arc is to be used, as for example when sectoring devices are used for analysis and calibration purposes (see Section 9–3).

Because of the sharp longitudinal intensity changes, accurate positioning of the arc source is critical when cathode layer excitation is employed. Not only does line intensity change rapidly but lines of different elements tend to have different intensity distributions (see for example Fig. 8–4). Kvalheim and Strock (1939) determined scandium in minerals (Section 17–1), using cathode layer excitation. At 0.033% Sc_2O_3, the intensity ratio of the analysis pair (Sc 4246 : La 4263) was 0.165 in the segment 2.0–2.9 mm from the cathode, whereas 1.1–2.0 mm from the cathode, the ratio changed to 0.09. If analysis and internal standard lines have the same intensity distribution, the ratio will of course remain constant at all points along the arc length.

CHAPTER 8

THE EFFECT OF A CHANGE OF COMPOSITION ON LINE INTENSITY

For quantitative analysis, standards are usually prepared from a base mixture whose chemical composition and physical properties resemble as closely as possible those of the specimens to be analyzed (Section 7–20). However, it is quite often necessary to analyze a variety of compositional types. Here a question arises as to whether for a given concentration of the analysis element the intensity of the analysis line (or the intensity ratio of the analysis pair if an internal standard has been used) will be affected by compositional changes. If such an effect is found to exist, it becomes necessary to prepare separate standards for each specimen type.

The consensus of several workers who have studied the problem is that the intensity of a line will frequently vary when composition changes. A relatively complete bibliography on this topic is given by Scott (1945) for publications up to that date.

8–1. Some examples of line intensity variations due to compositional changes. There are numerous examples of the effect of a compositional change on line intensity; a few are given and discussed in this chapter.

Scott (1945) has investigated line intensity changes for several elements (V, Cr, Co, Ni, Zr, Zn, La, Y, Ag, Cu, Cd, Mo, Bi, Ga, Sn, and Pb) and the ratios of their lines to those of iron, the internal standard, in bases of Al_2O_3, SiO_2, $CaCO_3$, $Ca_3(PO_4)_2$, $Na_4P_2O_7$, NaCl, and Na_2CO_3. Cathode layer excitation was employed. At a concentration of 0.0316% of each analysis element, line intensities and intensity ratios were measured and compared with the values in the alumina base. Table 8–1 gives the intensity and intensity ratio deviations, expressed in percents, from the values for the alumina base.

It should be clear from these data that line intensity is usually very sensitive to the composition of the matrix and that both anion and cation changes produce a marked effect on line intensity. The three sodium salts, pyrophosphate, carbonate, and chloride, create interesting results. The effects of sodium pyrophosphate and carbonate on line intensity are about the same, but that of sodium chloride is considerably different. Whereas pyrophosphate and carbonate depress the intensity of Zr 3391 relative to its intensity in the alumina base, its intensity is enhanced by the presence of the chloride. The presence of sodium chloride probably causes some

Table 8-1

(a)=% deviation for analysis element (b)=% deviation for internal standard (c)=% deviation for intensity ratio

	SiO_2			$CaCO_3$			$Ca_3(PO_4)_2$			$Na_4P_2O_7$			NaCl			Na_2CO_3		
	(a)	(b)	(c)	(a)	(b)	(c)	(a)	(b)	(c)	(a)	(b)	(c)	(a)	(b)	(c)	(a)	(b)	(c)
Co 3453 : Fe 3451	-10	-34	+33	-7	-24	+22	-9	-15	+7	-64	-66	+6	-8	-20	+14	-67	-72	+15
Ni 3414 : Fe 3413	+174	-24	+260	-9	-29	+28	-7	-15	+9	-60	-72	+35	-9	-31	+32	-56	-73	+62
V 3185 : Fe 3196	-99	-17	-98	+230	-27	+352	+185	-20	+257	-40	-65	+70	+16	-25	+54	-53	-72	+69
Mo 3170 : Fe 3196	-49	-17	-38	+7	-27	+47	+10	-20	+38	-50	-65	+42	-3	-25	+29	-55	-72	+62
Zr 3391 : Fe 3413	-32	-24	-7	+54	-29	+118	+50	-15	+77	-52	-72	+70	+22	-31	+78	-41	-73	+119
Ag 3280 : Fe 3305	-5	-31	+37	-5	-6	+2	-44	-21	-28	-53	-73	+73	-75	-36	-59	-55	-76	+95
Cu 3273 : Fe 3305	-16	-31	+21	-39	-6	-34	-34	-21	-16	-63	-73	+34	-72	-36	-56	-	-	-
Ga 2943 : Fe 2929	-52	-9	-48	+63	+2	+59	+6	+2	+4	+4	-57	+142	-43	-7	-38	-36	-63	+73
Sn 2839 : Fe 2838	-4	-32	+42	+21	-21	+54	-17	-19	+3	-54	-62	+21	-36	-9	-30	-41	-62	+53
Pb 2833 : Fe 2838	-36	-32	-5	-9	-21	+15	-45	-19	-18	-66	-62	-9	-44	-9	-36	-49	-62	+33

conversion to chlorides, thus volatilizing such very involatile elements as zirconium and causing them to enter the arc column more readily. The intensity of V 3185 is markedly increased in a matrix of $CaCO_3$. The ratio, $\frac{I \text{ Co } 3453}{I \text{ Fe } 3451}$ is remarkably stable, as is also the ratio $\frac{I \text{ Ag } 3280}{I \text{ Cu } 3273}$. For further comments see Scott (1945).

Most discussions on the possible causes of observed intensity changes due to compositional variations are highly speculative and qualitative. It would indeed be an aid to a better understanding of such intensity changes if observations were made at convenient intervals — perhaps every twenty seconds of the total arcing period — not only of the behavior of the analysis and internal standard lines, but also of lines of the major constituents. Intensity changes of major constituent lines would indicate the vapor composition of the arc column at each arcing interval. A temperature measurement of the arc at each interval is highly desirable. As observations invariably refer to a variation of *total* intensity of emission, they are very difficult to interpret.

Publications by Brode and Silverthorn (1939), Brode and Appleton (1940), and Churchill and Churchill (1941) record observations of the influence of compositional changes on line intensity in simple mixtures. Brode and Timma (1949) have described the effect of the addition one by one of other elements on line intensity of a single element. This investigation is of value because it makes possible the examination of the specific influence of each element on the line intensity of another. As a result of their investigations, these authors have placed several elements in sequence: Na, Sn, Fe, V, Al, Mn, Cd, Bi, Ca, Pb, Zn, and Cu. Each element will depress the line intensities of the elements listed to the right of it and enhance the line intensities of elements listed to its left. The authors observe that the influence of an added element is the same for all lines of a multiplet, but that each multiplet is affected to a different degree.

Brode (1943, pp. 127–131) discusses the influence of changes in composition on line intensity; several other examples of these effects will be found in Part II of this book and in Sections 8–2 to 8–7.

There are several possible causes for changes in line intensity when composition varies. These will be discussed in turn (Sections 8–2 to 8–7).

8–2. Volatilization. The manner in which an element volatilizes is usually altered by a compositional change. This effect can be extreme and elements otherwise involatile can be made volatile. Thus the presence of powdered carbon (or graphite) and ammonium salts speeds volatilization rates considerably (Section 6–3). If as a result of a change in composition a different anion is present, volatilization rates are likely to alter markedly

(Section 8–6). Although a compositional change will probably alter the intensity of emission over a given time interval, the total line intensity may not be affected, provided the specimen is arced to completion and the change of composition does not alter the arc temperature significantly. The fundamental requirement of the so-called "total energy" method (Section 7–18) is that the specimen be arced to completion, whereas internal standard methods sometimes use cutoff procedures. Consequently the "total energy" method is less sensitive to compositional changes and is more easily adapted to the analysis of a wide variety of substances. Furthermore, a method which employs internal standardization is usually more sensitive to compositional changes even if specimens are arced to completion because a ratio of intensities of two lines is used. Even if one is unaffected, the other might be altered, and the ratio would thus be disturbed. If the intensities of both lines of the analysis pair are affected, one may be enhanced and the other weakened, or, if they are affected in the same direction, it is unlikely that each will be altered to the same degree.

Silicon has been used as an internal standard for the analysis of iron in glass sands (Ahrens, 1944). The volatilization curves for iron and silicon in sand have been shown in Fig. 7–1, where iron is shown to be slightly more volatile than silicon. *Feldspar* is sometimes present in sand, and the alkali metals which it contains disturb the analysis pair intensity ratio. Thus if a potassium salt is added to a specimen of sand, the ratio $\frac{I \text{ Fe } 3020}{I \text{ Si } 2987}$ is altered considerably. This is shown in Fig. 8–1, a plot of $\frac{I \text{ Fe } 3020}{I \text{ Si } 2987}$ vs % potassium salt added to the specimen. Fig. 8–2, a plot of time vs I K 4047 and $\frac{I \text{ Fe } 3020}{I \text{ Si } 2987}$, shows that the intensity ratio is changed markedly only in the early period of arcing, during which the bulk of the potassium distills. During this period the volatilization rate of silicon relative to that of iron is strongly depressed and the ratio $\frac{I \text{ Fe } 3020}{I \text{ Si } 2987}$ is hence abnormally high. After the bulk of the silicon has volatilized, as evidenced by the sudden drop in intensity of K 4047, the ratio $\frac{I \text{ Fe } 3020}{I \text{ Si } 2987}$ alters sharply and becomes nearly normal.

In this example of the effect of a compositional change on the intensity ratio of an analysis pair, the influence of rate of volatilization may be regarded as the dominant contributing cause.

Borovik and Borovik-Romanova (1946) have investigated the analysis

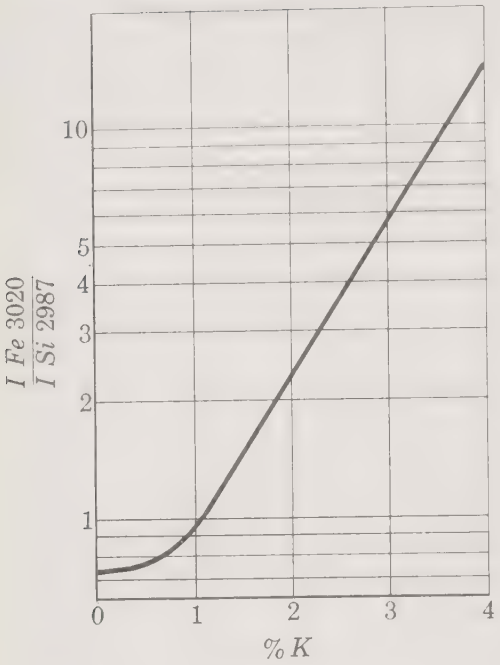

Fig. 8–1. The presence of potassium (>0.4%) is seen to enhance the ratio *I* Fe 3020/*I* Si 2987 very markedly. This is due to the depressant influence of potassium on the volatilization of silicon relative to iron. See Fig. 8–2.

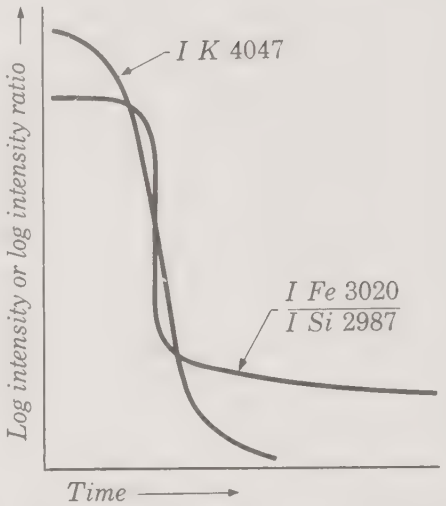

Fig. 8–2. The ratio *I* Fe 3020/*I* Si 2987 is high during the early period of arcing because much potassium vapor is present. After the volatilization of potassium, the intensity ratio drops sharply and remains nearly constant.

of lithium in soil. They observed that whereas the addition of Na_2HPO_4, CH_3COONa, $Na_2C_2O_4$, and Na_2CO_3 had no influence on the intensity of Li 6707, its intensity could be enhanced by the addition of NaCl and particularly KCl. The addition of one part of KCl enhanced the intensity of Li 6707 by a factor of six.

There are apparently two causes for the increase of intensity of Li 6707. First, in the presence of halide (NaCl compared with other sodium compounds) quicker volatilization increases intensity. Second, for common anion (NaCl compared with KCl) a temperature change is probably the cause (see Section 8–3).

8–3. Arc temperatures: Spectroscopic buffers. A change in the composition of the specimen will of course alter the composition of the arc gas and hence its effective ionization potential. This, in turn, will change the temperature of excitation. In the above example (Section 8–2) of the analysis of lithium in soil, KCl enhanced the intensity of Li 6707 more markedly than did NaCl. Li 6707 is a very low temperature line (excitation potential = 1.8 volts) and the lower arc temperature produced by potas-

sium vapor is more conducive to its emission than the somewhat higher arc temperature in sodium vapor.

If internal standardization has been attempted, the intensity ratio of the analysis pair will not be disturbed by a temperature change, provided their excitation potentials are similar. If the excitation potentials of the component lines differ considerably, however, the intensity ratio will be very sensitive to compositional changes. This applies in particular to an atom-ion line pair. The use of an atom-ion line pair *may* give poor reproducibility even if only one specimen type is analyzed (Section 7–5). If, however, a wide variety of compositional types are handled, the results will probably prove disastrous unless it has been possible to control arc temperature rigorously.

In an endeavor to compensate for changes in the excitation temperature of the source due to compositional variation, spectrochemists have introduced the *spectroscopic buffer*. When a mixture of elements enters the arc column, the element of lowest ionization potential is the most important in controlling arc temperature (Section 3–2). Therefore, in order to buffer successfully against temperature fluctuations in the arc source, a significant amount of an element of low ionization potential must be added to each specimen.

Because of their low ionization potentials, the alkali metals usually provide the most marked buffer action even when present in small amounts, and their compounds are in common use. It must be remembered, however, that they are volatile, and consequently their buffer action is restricted only to the early period of arcing. If all elements are present as halides, buffer action of the alkali metals is usually effective over a much larger portion of the total arcing period, because the halides of nearly all elements tend to be volatile. Many silicate minerals are self-buffered, at least during the early period of arcing, because they invariably contain appreciable amounts of sodium and potassium.

The term spectroscopic buffer is sometimes used loosely and may indicate any compound added in excess. In the stricter sense, it is concerned only with the buffering of temperature of excitation within the source by the constant presence of an element of relatively low ionization potential.

Calcium carbonate has quite often been successfully used as a spectroscopic buffer. In its presence the lines of many elements approach maximum intensity. The ionization potential of calcium (6.09 volts) is sufficiently low to make its use in the arc reasonably effective against temperature fluctuations due to compositional changes. The presence of large amounts of alkali metal, especially K, Rb, and Cs, may render calcium ineffective, however. In several respects calcium is a more satisfactory buffer than the alkali metals. Although the very low ionization potentials of the

alkali metals make the arc less sensitive to temperature changes, this buffering (as already noted) is usually restricted to the early period of arcing and it is often undesirable to have the main volatilization of relatively involatile elements suppressed until after the bulk of the alkali metals has distilled. On the other hand, calcium compounds are usually of medium volatility and as a result, their buffer action will persist over most of the arcing period without the tendency to suppress volatilization of other elements. The chief criticism against the use of calcium is its ineffectual buffer action against the alkali metals. Strontium and barium compounds may be used in place of calcium compounds.

Marks and Hall (1946) have made a study of line intensity changes in various matrices, using a method which did not employ an internal standard (Chapter 11). Anode excitation was used, and Sn, Pb, and Ge were sought in ores which contained Fe_2O_3, CaO, MgO, and Al_2O_3. The gangues of these ores were usually siliceous. The intensity variations of Sn 2840, Pb 2833, and Ge 3039 were noted in various proportions of the above oxides. The observations of these authors on Sn 2840 follow.

The intensity of Sn 2840 was found to vary considerably with composition of the base, and was greatest in alumina and calcium carbonate (Fig. 8–3). An attempt was consequently made to use calcium carbonate as a buffer, and this substance was added in excess to all specimens. Table 8–2 shows the variation of the intensity of Sn 2840 in various bases and the efficacy of calcium carbonate as a buffer. Column (a) shows the intensity changes of Sn 2840 in various matrices whose compositions are given, while (b) shows the behavior of Sn 2840 in these matrices after each has been diluted 1:1 with a $CaCO_3$-graphite mixture. 0.5% Sn, as SnO_2, is present in each specimen. In column (a) the highest intensities are present when $CaO + Al_2O_3$ are at a maximum.

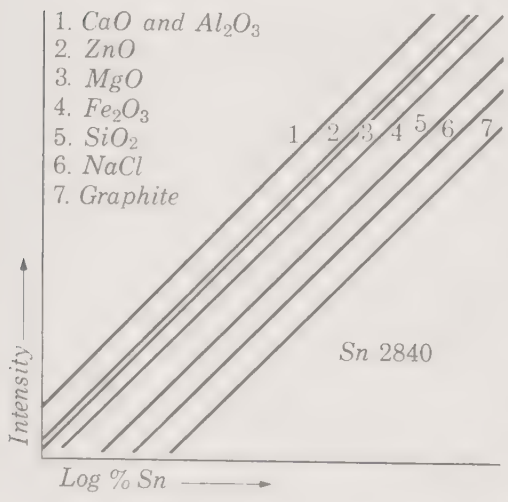

Fig. 8–3. The intensity of Sn 2840 is seen to change very markedly with the composition of the matrix. A maximum intensity is emitted in bases of Al_2O_3 and $CaCO_3$.

The mean intensity in (b) is 1.98, and all intensity values lie within ±6.0% of 1.98, a variation no greater than the experimental error. Consequently $CaCO_3$ has been effective as a buffer. Had it been necessary for Marks and Hall to

Table 8-2

Matrix Composition

SiO_2 %	Fe_2O_3 %	MgO %	CaO %	Al_2O_3 %	(a)	(b)
21.6	31.1	12.0	16.2	19.1	1.51	2.01
39.3	22.3	7.4	10.8	20.2	1.12	1.93
45.0	24.3	2.0	18.9	9.8	1.46	2.02
70.3	7.6	1.0	15.1	6.0	1.40	1.94
9.8	62.6	5.0	8.8	13.8	1.28	2.00
15.8	26.8	10.1	41.1	6.2	1.39	1.98
18.2	8.1	51.0	12.4	10.3	1.12	1.95
19.1	10.1	2.1	6.0	62.7	1.49	2.00
34.1	42.1	3.1	2.9	17.8	1.12	2.08
4.1	49.9	3.0	13.0	31.0	1.50	2.08
4.1	60.9	22.8	2.8	9.4	1.18	1.98
4.4	5.8	39.1	45.6	5.1	1.60	1.96
4.6	7.5	28.5	4.0	55.4	1.62	1.90
8.6	4.3	3.1	37.6	46.4	1.60	2.02
60.9	3.1	27.1	5.2	3.7	1.48	1.96
54.3	7.5	3.1	26.6	8.5	1.51	1.91
47.1	7.2	1.9	3.6	40.2	1.37	1.90
54.8	2.3	38.9	3.0	1.0	1.04	2.00
61.8	21.2	5.6	4.7	6.7	1.12	1.90
4.3	5.6	2.3	60.2	27.6	1.65	1.98

analyze tin in a gangue rich in potash feldspar, some difficulty might have been encountered, because the buffer action of calcium carbonate is rarely effective in the presence of the alkali metals, particularly K, Rb, and Cs.

The influence of a compositional change on line intensity may not be the same in both anode and cathode layer excitation. Unlike anode excitation, the success of cathode layer excitation depends largely on a relatively high and constant degree of ionization. When cathode layer excitation is used, a change in the degree of ionization is reflected by a sharp change in longitudinal intensity distribution in the arc. As a result, line response is more sensitive to a temperature change in the cathode layer arc than in the anode arc. See comments by Mannkopff (1933), Langstroth and McRae (1938), and van Tongeren (1938). Fig. 8–4 shows how the intensity distributions of Si 2528, the analysis line, and Be 2494, the internal standard line, vary when a rock specimen is arced in a small cathode and composition undergoes a change. The operating procedure is as given by Kvalheim (1947) for the analysis of silicon as a major constituent; the measurements are by Mrs. L. G. Gorfinkle of the Cabot Spectrographic Laboratory, M. I. T. Fig. 8–4 (1) shows the intensity distribution for the first thirty seconds of arcing, during which time much sodium and potassium vapor is present in the arc column. Fig. 8–4 (2) shows the intensity

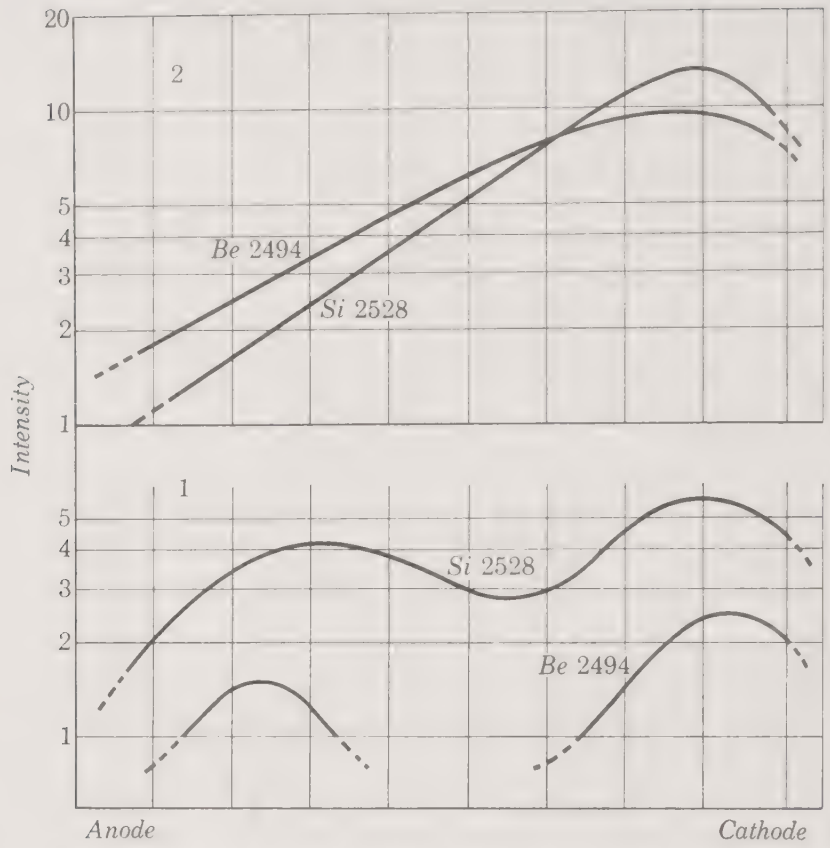

Fig. 8–4. Longitudinal intensity distribution of Si 2528 and Be 2494, using cathode excitation. In (1) much alkali metal vapor is present and there is a very slight development of cathode layer enrichment. In (2), no alkali metal vapor is present; degree of ionization is high because of higher temperature and cathode-layer enrichment is well developed. It is more marked in Si 2528 than in Be 2494.

distribution after sodium and potassium have volatilized. Not only does the intensity distribution for each line alter, but the intensity relationship between Si 2528 and Be 2494 is completely changed. Although Fig. 8–4 (1) shows only a relatively few measurements for Be 2494 because of the depressant influence of sodium and potassium on the volatilization of beryllium, the intensity of Be 2494 is seen to vary much more sympathetically with Si 2528 than it does in Fig. 8–4 (2). The reason is that in the presence of sodium and potassium vapor the temperature is relatively low and there is very little ionization. Thus only a negligible amount of ionic migration and enrichment occurs. If temperature is high, ionization is significant and cathode layer enrichment develops. However, this development differs for elements of different ionization potential. The ionization potential of silicon is 8.11 volts, that of beryllium is 9.29 volts; as a result,

silicon is more highly ionized than beryllium and shows a more fully developed cathode layer enrichment effect (Fig. 8–4 (2)).

8–4. Collisions of the second kind. Once excited, atoms and ions can lose part of their energy by collisions of the second kind (Section 2–9). Compositional changes alter the type and number of such collisions and may affect line intensity. The conditions most favorable to energy transfers caused by collisions of the second kind were given in Section 2–9. Duffendack, Wiley, and Owens (1935) were some of the first analysts to recognize the importance of collisions of the second kind in spectrochemical analysis. Physicists have observed energy level interactions when composition is altered under conditions of excitation not very different from those normally employed for spectrochemical analysis. Thus, Subbaraya, Seshadri, and Rao (1940) observed the relative intensities of the spectra of zinc and cadmium when excited alone and when excited as a mixture under closely controlled conditions of excitation.

In the zinc spectrum, Zn 3076 (upper level, 32501.6 cm^{-1}) was enhanced and Zn 2800, 2770, and 2756 (upper states: 68582.9, 68580.9, and 68579.8 cm^{-1} respectively) were decreased in intensity when emitted from the Zn: Cd mixture. Cadmium has a metastable state (31827.3 cm^{-1}) and line intensity enhancement of Zn 3076 is apparently attributable to interaction of unexcited zinc atoms with cadmium atoms in the metastable state. The weakening of Zn 2800, 2770, and 2756 is attributable to interaction of excited zinc atoms and unexcited cadmium atoms, which go to 67997.5, 67992.5, and 67988.9 cm^{-1} states. These are the respective upper levels for the Cd lines 2764, 2677, and 2640 and each of these showed an enhancement of intensity in the presence of zinc.

An example of an extreme change in emission intensity brought about by interaction of energy levels is given by Popov (1943). He shows that as a result of the interaction of certain calcium energy levels with metastable mercury levels, some calcium lines may be intensified by as much as 600–800× in the presence of mercury vapor. The source of excitation was a hollow cathode discharge.

8–5. Atomic and molecular weights of particles in the arc column. A change of specimen composition will cause a release into the arc column of atoms and molecules which differ in number and in atomic and molecular weight. This may affect intensity of line emission (see Langstroth and McRae, 1938).

8–6. The role of anions. Because elements which behave as typical anions in most compounds have extremely high ionization potentials,

their presence in the arc column does not influence temperature. As a result, typical nonmetals have no influence on the energy of the arc when composition changes. They may, however, influence line intensity in other ways. Several of the nonmetals — oxygen and some of the halides, for example — form relatively stable molecular complexes with metals in the arc and thereby decrease the number of metal atoms available for line emission.

The rate of volatilization of an element from the electrode cavity depends to a considerable extent on the anion to which it is bonded. A change of anion therefore is likely to alter volatilization rates and, as a consequence, influence line intensity (Section 8–1). Thus, by the addition of sodium chloride to a specimen, some elements are in part converted to the chloride when the arc is started and many elements otherwise involatile become much more volatile as a result of this conversion.

Brode and Hodge (1941) have examined the effect of anion variation on the emission of line intensity from certain compounds. Different calcium salts were added and the observation was made that those which produce stable molecular emitters in the arc cause the greatest depression of line intensity. Of the calcium halides, calcium fluoride was most effective in weakening line intensity, whereas calcium iodide produced the smallest effect.

8–7. Crystal structure. Line intensity may vary with crystal structure as well as with chemical composition. The type of bonding and the melting point differences affect volatilization rates and thus influence line intensity. Some spectrochemists recommend the use of a flux to break down crystal structure. Fusion of the sample can be carried out in the hot electrode cavity itself or in a suitable crucible, from which it may be transferred to the electrode cavity for analysis. Borax, the carbonates of the alkali metals, and germanium (Strock, 1948a) have been employed as fluxes.

One example of a large variation in intensity and sensitivity is that given by Oftedal (1941) for mercury in *sphalerite* (ZnS) and in ZnS precipitated in the laboratory. In *sphalerite* the detection limit for mercury was 10× lower than in laboratory precipitated ZnS.

8–8. Compositional effect in qualitative analysis. Although the effect on line intensity of a change in composition is invariably considered in quantitative analysis, its importance in qualitative analysis should not be overlooked. Frequently concentrations border on detection limits, and addition of the correct compound may make a particular element readily detectable. Thus, KCl may be added to soils to attain the lowest detection limit for lithium, and $CaCO_3$ may be added for detecting the lowest concentration of vanadium (see Table 8–1). There are of course many other examples; some appear in Part II.

CHAPTER 9

THE PHOTOGRAPHIC MEASUREMENT OF RADIANT ENERGY AND THE CONSTRUCTION OF A WORKING CURVE

In quantitative spectrochemical analysis, relative intensity changes must be measured. Because photographic emulsion is used in recording spectra, it is necessary to examine closely the *response* of this emulsion to intensity changes of incident radiation.

When discussing the photographic response to incident radiant energy, *exposure* (E) is commonly used, where $E = I \times t$ (t = time of exposure of intensity I). In quantitative spectrochemical analysis, the photographic emulsion receives exposure variations in which t is constant for a given procedure and I varies.

In this book no description is given of darkroom procedures. For such a description see Brode (1943, pp. 361–370), Sawyer (1944, pp. 195–200), and Harrison, Lord, and Loofbourow (1948, pp. 153–158). Harrison, Lord and Loofbourow list references to several texts on photography.

9–1. The microphotometer, density, and the calibration curve. A microphotometer, known also as a densitometer, is used to measure photographic response accurately. Operational details are given by Harrison, Lord, and Loofbourow (1948, pp. 350–361), Sawyer (1944), and Brode (1943). Very briefly, the instrument operates on the following principles. A narrow light beam of constant intensity i_0* is passed through an exposed region of the plate to be measured; for our purpose the exposed region will be a spectral line. The transmitted light of intensity i then activates a photocell whose current response is recorded by a galvanometer swing or deflection (d) across a scale. This scale usually has 100 or 50 divisions.

The weight of silver produced per unit area in a developed image is closely proportional to the ratio $\log \frac{i_0}{i}$ usually known as *density* (D). Density is of fundamental significance and is commonly employed as a measure of photographic response. Because of the existence of a linear relationship between the intensity of light incident on the microphotometer photocell and the galvanometer deflection,

$$D = \log \frac{i_0}{i} = \log \frac{d_0 - d_\bullet}{d - d_\bullet},$$

* Lower case i_0 and i are used here so as not to confuse with the I_0 and I used elsewhere in this book, where they refer to spectral lines. In many books and publications capitals are used for both purposes.

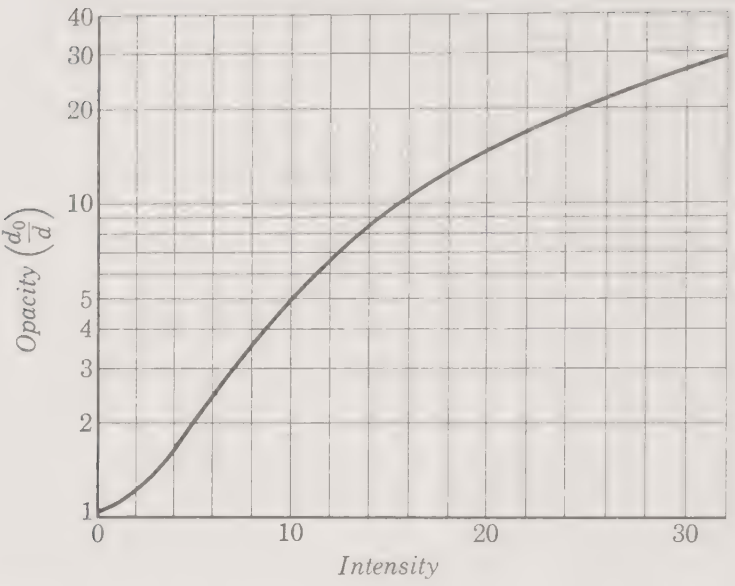

Fig. 9–1. An example of a calibration curve; not generally used, but of value for the determination of weak intensities.

where d_0 is the galvanometer deflection for i_0 (equivalent to the light transmitted by a perfectly clear area on the photographic plate (or film) which has received no light exposure) and $d_\bullet$ is the deflection when no light reaches the photocell.

For convenience the scale is usually adjusted for $d_\bullet = 0$. Then

$$D = \log \frac{d_0}{d}$$

The antilog of density is known as *opacity* (O).

If different areas of the photographic plate are exposed to different known intensities (as described in Section 9–3) a plot of density vs intensity gives a *calibration* curve (Fig. 9–1). It is more common to plot density vs log intensity, and the resultant graph usually shows a curve like that in Fig. 9–2 (1). This particular calibration curve is known as a *characteristic* or H and D (after Hurter and Driffield) curve (Section 9–2). For convenience it is customary to use log-log coordinates. The characteristic curve is drawn from a plot of opacity vs intensity.

Any response vs intensity relationship may serve for plate calibration, but a smooth curve, preferably one with a long straight line portion, is usually used (Fig. 9–2). If the microphotometer clear glass deflection is held constant at 100 scale divisions, then as a measure of photographic response, log d is somewhat more convenient to plot than log d_0/d. Fig. 9–2 (2) shows a plot of log d vs log intensity; the curve is the inverse of that in Fig. 9–2 (1).

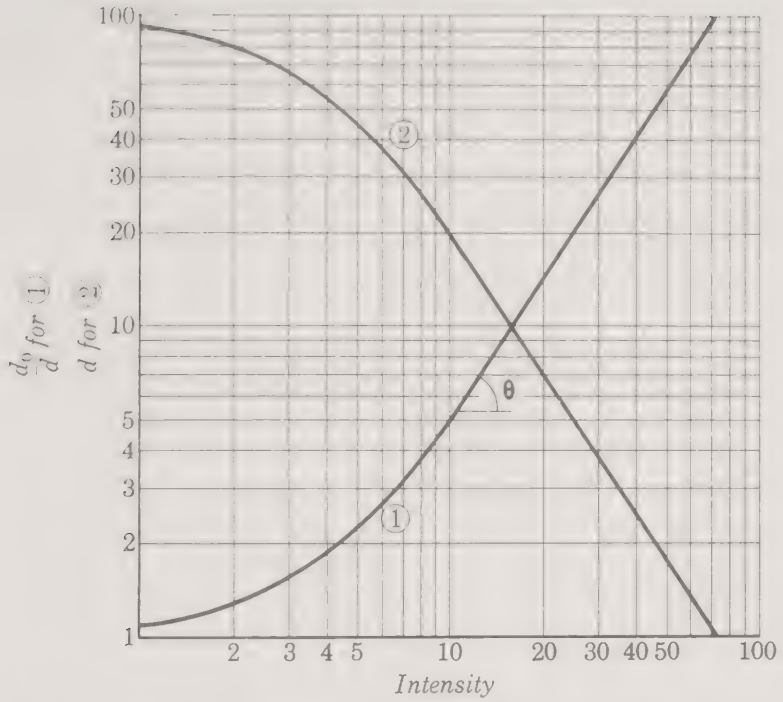

Fig. 9–2. Examples of commonly used calibration curves. (1) is known as a *characteristic* (or H and D) curve. (2) has the same form but its position is reversed.

The characteristic curve may also be drawn by plotting *log per cent transmission* (T) vs log intensity:

$$T = \frac{i}{i_0} \text{ and consequently } D = \log \frac{1}{T}.$$

If the clear glass deflection of 100 divisions is equivalent to 100% transmission, each deflection for an exposed area is a measure of per cent transmitted. If then a plot is made of log d (on ordinate, with log 100 as base) vs log I, a characteristic curve is obtained. For convenience, d (per cent transmission) vs I is usually plotted on log-log coordinates. Plots of either D or log d vs log I are those most commonly used for plate calibration. Each plot gives the form of the characteristic (H and D) curve. Not only do these plots provide a straight line relationship over a relatively large range of photographic response, but they also give information about plate *gamma* (Section 9–2) which may be seen at a glance.

Blackening ($d_0 - d$) is also sometimes used as a measure of photographic response, and a $d_0 - d$ vs log intensity plot is shown in Fig. 9–3. This curve also shows a straight line portion which covers lower response values than does the characteristic curve.

For the measurement of low intensities, that is, those corresponding to densities of 0.2–0.3 or less (corresponding deflections 65.0–50.0, when

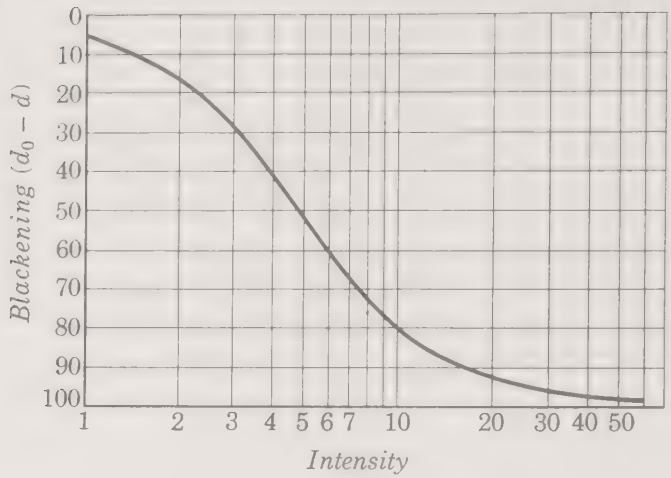

Fig. 9–3. An example of a calibration curve where *blackening* is used as a measure of photographic response. Not in very common use.

$d_0 = 100$) which lie on the toe of the characteristic curve, it is more convenient to use a plot of density vs intensity (Fig. 9–1). Such curves are much steeper at low response values, and their equivalent intensities may thus be evaluated more accurately. Because the intensity level of background is usually restricted to this low response region, a D vs I plot may be conveniently used for background correction (Section 9–7).

Once a plate has been calibrated by means of a calibration curve, the photographic response of each spectral line may be converted to its equivalent relative intensity, which is of course the first object in quantitative spectrochemical analysis.

The deflection data used for the construction of the curves in Figs. 9–1, 9–2 (1) and (2), and 9–3 are the same, and these curves are thus directly comparable. Measurements were made on an Eastman 103–0 plate.

9–2. The characteristic curve. Not only is the characteristic curve commonly employed as a calibration curve in spectrochemical analysis, but it is also used to give meaning to many photographic terms used in describing the properties of emulsions. Consequently, it will be examined more closely here.

The straight portion (Fig. 9–2) is referred to as the *latitude*, and its slope, tan θ, is the *gamma* (γ); gamma is thus a measure of the contrast of the emulsion. For most plates used in spectrochemical analysis, gamma lies within the range of 1.0 and 2.0. A high value of gamma restricts the range of concentrations which may be measured accurately on the microphotometer. Relatively intense lines for which the microphotometer deflection is 2.0–3.0 divisions ($d_0 = 100$) or less cannot be measured

accurately on the microphotometer, nor are those lines which are relatively weak (deflections of about 70.0 or more) capable of accurate measurement. The accurately measurable response range is confined therefore to deflections of ~2.0–70.0. Expressed as density, the range is from 0.15–1.7. If the gamma of the plate is 1.5, such a range in photographic response corresponds to a change of 20 in intensity and hence in the relative concentration of the element. A factor of 20 is reasonably large for many purposes in quantitative spectrochemical analysis, but because of the wide ranges of concentration which are often encountered in rocks and minerals, an even wider latitude is sometimes desirable. If gamma is 1.0, a range of concentrations which varies by a factor of 50 may be handled. However, gamma should not be appreciably lower than 1.0. The advantage of a wider range of concentrations is offset by inaccuracy in measuring intensity changes, due to the very slight response of the photographic emulsion to intensity change. Gamma values between 1.0 and 1.5 are probably best suited for most mineral, rock, and soil analyses.

Gamma may also vary with wavelength. Fig. 9–4 shows two typical gamma vs wavelength curves, (1) for a plate of relatively high gamma, and (2) for one of relatively low contrast. In general, only the slow high-contrast emulsions which are used for quantitative analysis show large variations of gamma with wavelength. The typically fast low-contrast emulsions more generally used for qualitative analysis, and also quite frequently for quantitative analysis (see comments below), usually show very slight variations.

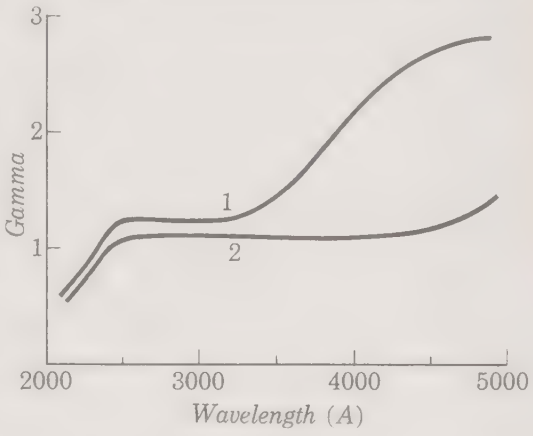

Fig. 9–4. Two typical gamma vs wavelength curves, (1) for a slow emulsion (Ilford Ordinary) and (2) for a fast emulsion (Spectrum Analysis No. 2).

For details on gamma:wavelength variations in various emulsion types, Amstein (1944) should be consulted. Data are provided on several Kodak and Ilford emulsion types. (Ilford Process, Thin Film Halftone, Ordinary, Special Rapid, Press, Zenith and Q1, and Kodak Slow Spectrographic, B5, B10, B20, 0120 and P25.) The author concludes that nearly all present-day emulsions have gamma constant between 2500 and about 3100 A. Consequently a single calibration curve suffices for the intensity measurements of lines at all wavelengths within this range. Davey and Gauntlett (1945) state that within this region (2500–3100 A) radiation is strongly

absorbed by the silver halide, which restricts the photographic image mainly to the surface of the plate. At longer wavelengths, deeper light penetration develops, causing an increase in contrast.

When an internal standard is to be selected, the difference in wavelength between analysis and internal standard lines must be considered. Ideally they should be closely spaced (Section 7–10), although a reasonable accuracy can usually be obtained even when the wavelength difference is considerable, provided that careful attention has been given to calibration. As already noted, gamma is constant between 2500 and 3100 A for most plates, and within this range a single calibration curve suffices even if the wavelength difference of the components of the analysis pair is several hundred A. Should gamma vary rapidly with wavelength and should the wavelength difference between analysis and internal standard lines differ significantly, two calibration curves must be drawn, one for each line. Relative intensities of the internal standard and analysis lines are read off from their respective calibration curves. Such double calibration enables the analyst to use lines at wavelengths with different gamma; some precision may be lost, however.

For the quantitative analysis of minerals, rocks, and soils, workers frequently tend to employ fast plates which would usually be regarded as qualitative. There are several reasons for this. First, the need for highest sensitivity is often great. Second, as already noted above, relatively large concentration ranges often must be analyzed and for this purpose the typically quantitative high contrast plates impose severe limitations. Third, wide wavelength ranges are often covered because large numbers of elements are frequently sought; consequently, plates which have fairly uniform gamma are preferred to those which show sharp increase in gamma above 3100–3200 A. When using fast, coarse-grained emulsions, accuracy is usually adequate for most purposes and the loss of precision is small compared with the experimental error. Thus, in many methods for which standard deviations as good as ± 3.5–5.0% have been reported, comparatively fast, "qualitative" plates have been used. Background interference is usually greater when fast plates are used and for the measurement of the intensity of a weak line in a heavy background a plate which has a high gamma should be employed.

In the U. S. the most commonly used plates for spectrochemical analysis are manufactured by the Eastman Kodak Company, Rochester, New York. Two fast emulsion types which are suitable also for quantitative analysis are the Eastman 103–0 and Spectrum Analysis No. 2 plates. These are not sensitized plates and are sensitive therefore only in the blue and ultraviolet. Both plates show only a very slight change of gamma with change of wavelength. For work at longer wavelengths panchromatic emulsions

have to be used. For a description of all available emulsion types for spectrochemical analysis, consult the recent editions of *Photographic Plates for Use in Spectroscopy and Astronomy*, obtainable from the Eastman Kodak Company.

British workers usually employ plates made by the Ilford Company, England. The Ilford Zenith plate is very sensitive, and is much used for qualitative and some quantitative work. The Ilford Ordinary plate is slower and is generally used for quantitative work. Ilford Long Range Spectrum is a plate that is reasonably sensitive up to 8500 A and is a useful general plate.

In Europe spectrochemists have employed Agfa, Perutz and Gavaert plates.

Part of the total error of a determination is due to the microphotometric measurement. To lessen the microphotometric error the use of broad lines has been recommended and this, of course, necessitates the use of a broad slit. A broad slit is not objectionable provided the spectrum of the mineral, rock, or soil is relatively simple, but its use is limited by the complexity of the spectra of many specimens. Consequently slit widths of 0.015–0.03 mm are commonly employed. No serious difficulties in the microphotometric measurement of relatively narrow lines are found, however, and microphotometric errors are invariably small compared with experimental errors. Because of the fineness of the grain of high-contrast emulsions, microphotometric errors are usually somewhat less for typically quantitative plates than for coarse-grained fast plates. In general, the microphotometric error, expressed as a standard deviation, is approximately ± 1–2%.

9–3. Recording a graded series of intensities for the construction of a calibration curve. Harrison (1934) lists numerous methods for obtaining an intensity (or time of exposure) variation which may be used for the purpose of plate calibration. These are given in Table 9–1, which is adapted from his paper. The footnotes are the author's.

Of the many possible methods for obtaining a graded series of relative intensities, or times of exposures, comparatively few are commonly employed for spectrochemical analysis. Most of these are underscored in Table 9–1. Of these few, the rotating step sector is in most common use. Such a sector usually contains from four to seven steps. It is cut in such a way that a graded series of exposures is allowed to reach the plate stepwise when the sector is rotated rapidly immediately in front of the spectrograph slit. The step aperture ratios are constant and frequently = 2.0. Any step factor can of course be used, provided it is accurately known. Usually a source rich in lines, such as an iron arc, is used in conjunction

any region of arc. Transmitted radiation is intercepted in front of the slit by a long-focus spherical lens which is in focus at the collimator. This setup provides intense illumination and has been recommended by Twyman and Simeon (1930); see also Strock (1936b) and Pierce, Torres, and Marshall (1940).

(5) Two cylindrical lenses. The first throws a vertical line of light on the slit only in the horizontal direction, and the second lens, with its axis at right angles to that of the first, throws an image on the collimator as a horizontal band of light. See Harrison, Lord, and Loofbourow (1948, p. 129) for details about this method.

(6) A method recommended by the Zeiss firm, using three spherical lenses. See Rankama and Joensuu (1946).

(7) Helz and Scribner (1947) have recommended the use of a ground quartz plate as an aid to obtaining uniform slit illumination.

Of these methods, Nos. (2), (4), and (5) are in most common use.

Uniform slit illumination is required for any device which alters exposure time or intensity along the length of the slit.

A step weakener (filter) or wedge at the slit is sometimes used to avoid any possible errors due to the failure of the reciprocity law or to an intermittency effect. Unfortunately no truly neutral weakener is obtainable, because no substance which reduces light uniformly throughout the spectrum is known. These weakeners require calibration at various wavelengths, but once this is done they are convenient to use (see discussion by Kaiser, 1949).

Effective use has been made of the so-called step slit. The usual slit is replaced by one with various widths arranged as a series of steps. Continuous radiation is generally employed, though on occasion a line can be used, provided its width is greater than that of the slit. If continuous radiation has been used, a series of bands is obtained on the spectrogram. Because of the possibility that the characteristic curve for continuous radiation may not be exactly the same as that for line emission (Section 9–7), the use of this method may introduce some error. It is difficult to accurately construct step slits.

The use of a group of lines of known relative intensity is quickly becoming a popular method of obtaining a graded series of intensities on the plate. All members of such a group should have similar excitation characteristics so as to render their intensity relationships constant and independent of source variations. Consequently, the components of a multiplet group are best suited for this purpose. In some instances it is possible to use theoretical intensities as calculated from the sum rule. If the relative intensities of the multiplet components do not accord with theory, the multiplet may nevertheless be used provided the relative intensities of the component lines are first accurately determined with the aid of some other primary method of calibration.

Dieke and Crosswhite (1943) have examined the relative intensities of components of some multiplets of iron with a view to their use in plate calibration. An iron arc was used as a source. Dieke and Crosswhite found that a major source of difficulty was the presence of self-absorption in low level lines. Low-level multiplets must therefore be avoided, even if a low amperage arc is employed. The multiplet which ends in the z^7D level* was found satisfactory, and lines which were comparatively intense were free from self-absorption. The low-level energy of lines in this multiplet is 2.4 volts. Dieke and Crosswhite give the relative intensities of the lines of this group but mention that due to some systematic error the values are not accurate. The present author has determined the relative intensities of several of the lines, using step sector calibration. Table 9–2 gives these values, calculated on the intensity of Fe 3217.3 = 1.0.

Table 9-2

λ	I
3160.6	0.63
3161.9	0.36
3175.4	0.69
3178.0	0.52
3200.4	1.65
3205.3	1.34
3215.9	1.50
3217.3	1.00
3222.0	4.90
3239.4	2.22
3244.1	1.93

Although some of these lines have wavelengths of 3200 A or a little more, the group can be employed in the wavelength range of 2500–3200 A for many emulsion types. Despite the fact that these lines have been called free from self-absorption, observations on an iron arc between two iron electrodes at 3 amp (made in the Cabot Spectrographic Laboratory, M.I.T.) have indicated very definitely that self-absorption sometimes appears. It is probably safer, then, to use some substance in which iron is not present as a major constituent.

To overcome the danger of self-absorption as a result of a high vapor density of iron in an iron arc, a small amount of an iron compound may be incorporated into a base which burns very smoothly. Such a procedure is adopted at the U. S. Geological Survey Laboratory, where a *quartz-feldspar* base is used. A carbon powder diluent, mixed with iron oxide, has also been used in some laboratories.

Should iron be present as a minor constituent, several of the other multiplets listed by Dieke and Crosswhite may be used. The spectra of many common rock-forming minerals and rocks contain a sufficient con-

* The use of lines of the $a^7D - x^7D$ multiplet for plate calibration has been investigated by Vorontsov-Vel'yaminov and Murasheva (1943).

centration of iron for calibration purposes. If the specimen itself is used, it is not necessary to employ a special source for calibration (Dennen, 1949). Frerichs (1926) has given relative intensity measurements on many multiplets of iron.

The spectra of manganese and titanium are both rich in multiplet groups. Because both elements are commonly present in appreciable concentrations in numerous minerals and rocks, many lines of their respective spectra are often in evidence. The relative intensities of the lines composing several of their multiplets have been determined. Seward (1931) has investigated the relative intensities of the manganese spectrum and Harrison (1928) those of the titanium spectrum. The use of manganese or titanium multiplets seems quite feasible for plate calibration; manganese in particular has many conveniently placed multiplets whose component lines show a good intensity range.

Even if only two lines of known relative intensity are available, they may be used for the calibration of the straight-line portion of the characteristic curve. Thus the doublet K 4044–4047 has been employed by workers in the Cabot Spectrographic Laboratory, M. I. T., for the calibration of the 4100 A region. The ratio $\frac{I\ 4044}{I\ 4047}$ is exactly 2.0. The absence of self-absorption must first be established and the intensities of the two lines must fall on the linear part of the characteristic curve; for most emulsions, their densities should be at least 0.3 or more. The presence or absence of self-absorption in the lines of a multiplet may be ascertained as described in Section 7–9.

A method of plate calibration has been described by Churchill (1944), which requires the use of only two lines. In this case the intensity ratio should lie between 1.2 and 2.0. (Details are to be found in Churchill's paper.) This method has promise of wide application; it appears simple and accurate. A basic assumption is that the intensity ratio of the calibration line pair remains constant; ideally, therefore, each line should have the same multiplet assignment. Churchill's procedure has been named the *two-line* method.

For comments on and discussion of the use of some other methods of plate calibration, see Harrison, Lord, and Loofbourow (1948, pp. 330–342). Additional bibliography is given there.

9–4. The working curve. As usually understood, a *working curve* is the curve obtained from a plot of the intensity of the analysis line, or the intensity ratio of the analysis pair, vs the concentration of the analysis element in each of a series of standards. The calibration curve is employed to convert line response values to intensities; when the working curve is

Table 9-3

	(1)		(2)		(3)		(4)
	d		d_o/d		I		Ratio
$\%K_2O$	K 4047	Rb 4202	K 4047	Rb 4202	K 4047	Rb 4202	$\frac{I\ K\ 4047}{I\ Rb\ 4202}$
	1.8	5.7	34.4	10.9	4.08	2.23	2.1
7.5	2.3	5.3	27.0	11.7	3.95	2.35	1.74
	2.6	6.6	23.8	9.4	3.72	2.03	1.83
	1.8	2.6	34.4	23.8	4.80	3.72	1.29
5.0	2.5	4.7	24.8	13.2	3.85	2.56	1.50
	3.5	6.4	17.7	9.7	3.08	2.08	1.48
	6.3	6.8	9.84	9.1	2.08	1.97	1.05
2.5	5.8	7.0	10.7	8.9	2.21	1.95	1.13
	5.8	6.6	10.7	9.4	2.21	2.03	1.09
	10.5	6.8	5.90	9.1	1.49	1.97	0.75
1.5	12.2	8.1	5.08	7.7	1.35	1.77	0.76
	14.2	9.8	4.37	6.3	1.21	1.56	0.78
	16.5	6.8	3.76	9.1	1.08	1.97	0.55
1.0	24.4	10.4	2.54	6.0	0.79	1.49	0.53
	23.0	10.2	2.69	6.1	0.82	1.52	0.54
	26.8	3.6	2.32	17.2	0.72	3.03	0.24
0.4	28.9	4.2	2.14	14.8	0.69	2.70	0.26
	35.6	6.2	1.74	10.0	0.56	2.10	0.27
	53.0	6.7	1.15	9.3	0.22	2.00	0.11
0.1	54.8	8.7	1.13	7.1	0.21	1.68	0.12
	47.2	4.8	1.31	12.9	0.33	2.50	0.13

(Exposure time, 30 seconds).

$d_o = 62.0$

plotted it is customary to employ log-log co-ordinates. Table 9–3 provides some data which have been used for the preparation of a working curve, in this case for the determination of potassium in *plagioclase feldspar*, using rubidium as the internal standard. The analysis pair is K 4047:Rb 4202. The measurements have been made by F. C. Canney at Cabot Spectrographic Laboratory, M. I. T. All the necessary data are given in Table 9–3. The numbers (1), (2), etc., at the head of each column give the order in which measurements and calculations are made. If the calibration curve employed is a plot of log d vs log I, the calculation of d_0/d in step (2) will of course not be made. Or if the calibration curve is a plot of $d_0 - d$ vs log I, substitute this for d_0/d in (2). No conversions to logarithms are

centration of iron for calibration purposes. If the specimen itself is used, it is not necessary to employ a special source for calibration (Dennen, 1949). Frerichs (1926) has given relative intensity measurements on many multiplets of iron.

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Table 9-3

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	$\frac{d}{}$		$\frac{d_o}{d}$		$\frac{I}{}$		Ratio
$\%K_2O$	K 4047	Rb 4202	K 4047	Rb 4202	K 4047	Rb 4202	$\frac{I\ K\ 4047}{I\ Rb\ 4202}$
	1.8	5.7	34.4	10.9	4.08	2.23	2.1
7.5	2.3	5.3	27.0	11.7	3.95	2.35	1.74
	2.6	6.6	23.8	9.4	3.72	2.03	1.83
	1.8	2.6	34.4	23.8	4.80	3.72	1.29
5.0	2.5	4.7	24.8	13.2	3.85	2.56	1.50
	3.5	6.4	17.7	9.7	3.08	2.08	1.48
	6.3	6.8	9.84	9.1	2.08	1.97	1.05
2.5	5.8	7.0	10.7	8.9	2.21	1.95	1.13
	5.8	6.6	10.7	9.4	2.21	2.03	1.09
	10.5	6.8	5.90	9.1	1.49	1.97	0.75
1.5	12.2	8.1	5.08	7.7	1.35	1.77	0.76
	14.2	9.8	4.37	6.3	1.21	1.56	0.78
	16.5	6.8	3.76	9.1	1.08	1.97	0.55
1.0	24.4	10.4	2.54	6.0	0.79	1.49	0.53
	23.0	10.2	2.69	6.1	0.82	1.52	0.54
	26.8	3.6	2.32	17.2	0.72	3.03	0.24
0.4	28.9	4.2	2.14	14.8	0.69	2.70	0.26
	35.6	6.2	1.74	10.0	0.56	2.10	0.27
	53.0	6.7	1.15	9.3	0.22	2.00	0.11
0.1	54.8	8.7	1.13	7.1	0.21	1.68	0.12
	47.2	4.8	1.31	12.9	0.33	2.50	0.13

(Exposure time, 30 seconds).

$d_o = 62.0$

plotted it is customary to employ log-log co-ordinates. Table 9–3 provides some data which have been used for the preparation of a working curve, in this case for the determination of potassium in *plagioclase feldspar*, using rubidium as the internal standard. The analysis pair is K 4047:Rb 4202. The measurements have been made by F. C. Canney at Cabot Spectrographic Laboratory, M. I. T. All the necessary data are given in Table 9–3. The numbers (1), (2), etc., at the head of each column give the order in which measurements and calculations are made. If the calibration curve employed is a plot of log d vs log I, the calculation of d_0/d in step (2) will of course not be made. Or if the calibration curve is a plot of $d_0 - d$ vs log I, substitute this for d_0/d in (2). No conversions to logarithms are

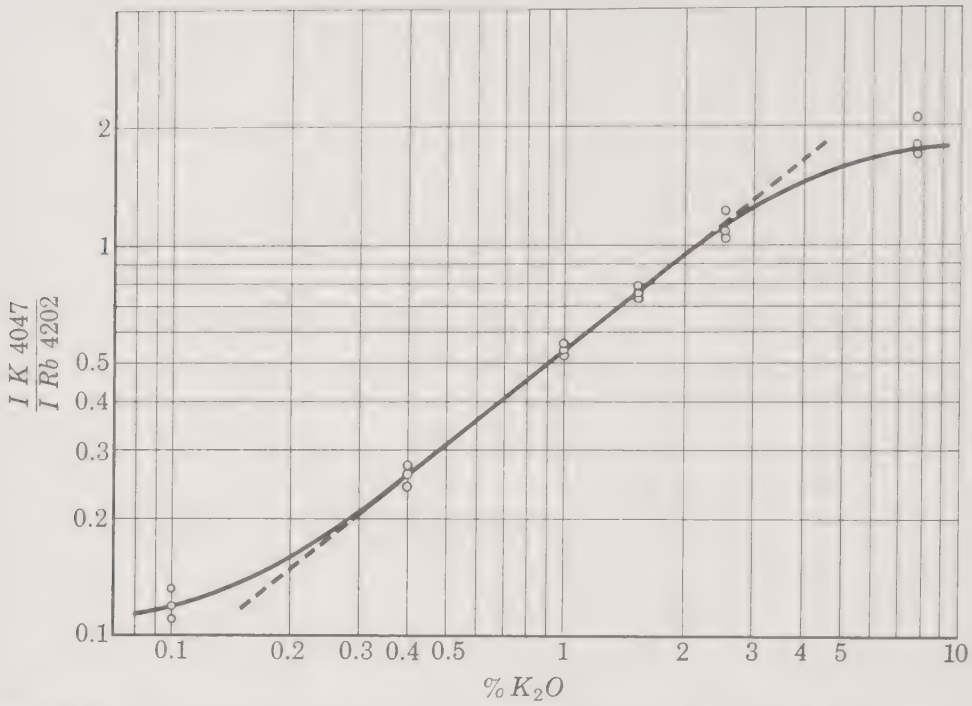

Fig. 9–5. A typical working curve. Self-absorption is evident above a concentration greater than about 2.5% K_2O. This working curve has been used for the determination of potassium in feldspar (Section 23–3).

given in Table 9–3 because it is assumed that calibration and working curves have been made on log-log paper.

Fig. 9–5 shows the working curve obtained through the use of the data in Table 9–3. This curve is used for determining potash in the unknowns. For the analysis of an unknown the procedure is exactly the same as for the determination of intensity ratios outlined above. By referring the intensity ratio of the line pair to Fig. 9–5, the corresponding potash content may be read off.

At relatively high potash contents, K 4047 shows some self-absorption. Extreme spreading of the plotted points may be observed at these relatively high concentrations. At low concentrations there is a deviation from linearity because of the greater contribution of background intensity to the measured intensity.

It is sometimes possible to dispense with the use of several standards. Provided the concentration of the analysis element in the unknowns is of a magnitude similar to that in the standard and does not vary strongly, one standard may suffice. Thus, for example, a single diabase rock standard for gallium has been employed for the analysis of gallium in several other diabase specimens. The standard specimen is arced several times and the intensity ratio of the analysis pair is thus accurately determined. A plot

is made of this ratio vs % Ga_2O_3 (log-log co-ordinates), and a short straight line of unit slope is drawn through the plotted point (Fig. 9–6). This curve is a short *single-point working curve* which may be used for the estimation of gallium in other specimens of diabase. Fig. 15–1 records the spread of the Ga_2O_3 concentration in 33 diabase specimens. Since this variation is small, no serious error is introduced by the use of a single-point working curve of unit slope. Naturally this short-cut method cannot be used where the analysis element varies considerably. Before attempting this procedure, the analyst should satisfy himself that the analysis line is free from self-absorption.

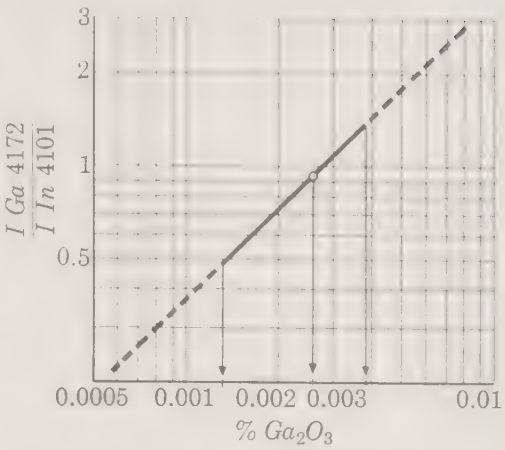

Fig. 9–6. An example of a *single-point* working curve. May be employed for the analysis of unknowns over a imited range of concentration, as indicated by the solid curve. The plotted point is a mean of several intensity ratio determinations and the slope of the working curve is arbitrarily chosen as 45°.

Use may sometimes be made of the so-called *addition method* as a means of determining the concentration in an unknown. Here the unknown itself is used as the base material. A compound of the element sought is added to the unknown and at least two standards are prepared, in which the amount added is usually made to vary by a factor of about two. If $a\%$ = concentration of the element sought in the unknown and $x\%$ and $2x\%$ are added, the standards will have $(a + x)\%$ and $(a + 2x)\%$ of the element sought. A plot is made of % element added vs intensity of analysis line (or intensity ratio of the analysis pair if an internal standard has been used) using ordinary co-ordinates. The unknown is included in this plot and is of course equivalent to the plot of 0% of added material. Fig. 9–7 shows the method of plotting. (Measurements by K. Bell of the Cabot Spectrographic Laboratory.) If the points all fall on a straight line, an extrapolation may be made. The intercept of this extrapolation with the abscissa gives the concentration of the element sought in the unknown. In this example it was desired to know the concentration of Ga_2O_3 in a specimen of alumina which was being used as a base material for synthetic standards. Fig. 9–7 shows this concentration to be 0.0012% Ga_2O_3.

A few points should be borne in mind when using the addition method. First, self-absorption must be absent. This may be checked by plotting at least *three* points (Fig. 9–7) and observing whether or not there is linearity. Second, the compound added will very likely differ from that which contains

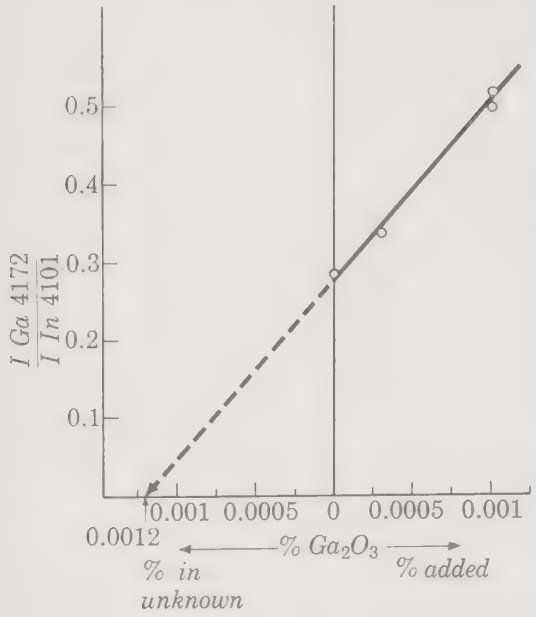

Fig. 9–7. This diagram illustrates the *addition method* of determining the concentration of an element in an unknown. In this example, extrapolation of the solid line curve shows 0.0012% Ga_2O_3 in a specimen of alumina.

the element sought in the unknown. Because of the compositional difference (Chapter 8) the point for the unknown (0% added) may be displaced with respect to a line drawn through the plotted points for the standards. Third, correction should be made for background if it is appreciable; otherwise the slope of the curve will decrease and extrapolation will give an excessively high result.

For some references to the use of the addition method, see Oertel (1944). See also analysis of rubidium (Section 12–2).

9–5. Other methods of obtaining intensities and the working curve. The general procedure outlined in the first part of Section 9–4 is the one most commonly employed. Two others, which make use of a microphotometer, will also be described.

The first of these may be termed a *self-calibrating* method. A step sector is rotated in front of the slit for each analysis exposure. In place of the step sector, any device which provides a graded exposure pattern along the slit length may be used. The optical setup is the same as that used for step sector plate calibration and No. (2), (4), or (5) (Section 9–3) is usually used.

Consider a determination of the ratio $\frac{I\ \text{Sr}\ 4077}{I\ \text{Rb}\ 4202}$ in a step spectrogram (see Ahrens, 1949). In each specimen rubidium is relatively constant and may be regarded as the internal standard.

A partial characteristic curve for 2 or 3 sector steps is drawn for the analysis and internal standard lines of each specimen (Fig. 9–8) and if necessary for background (Section 9–7) adjacent to each line. The separation of the internal standard and analysis lines at a given density is a measure of the relative exposure ratio of the two lines. The density value should lie on the straight-line part of the characteristic curve; a value of 1.0 (= opacity of 10) is convenient. If possible reciprocity and inter-

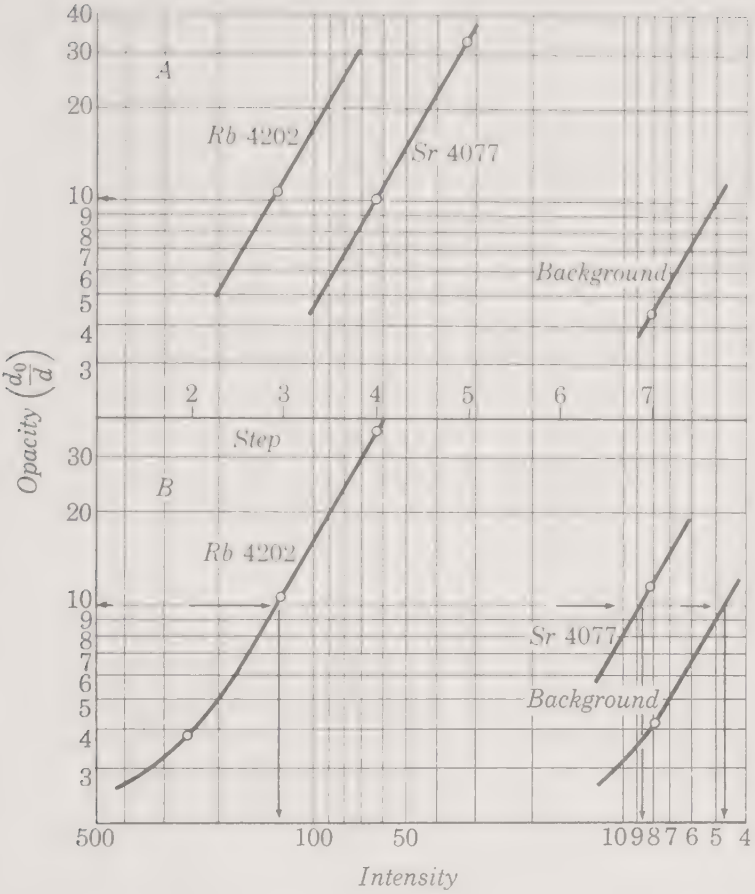

Fig. 9–8. This figure illustrates the determination of intensity ratios by the self-calibration method. Partial characteristic curves are drawn, using opacity measurements at convenient sector steps (2,3,4, . . . etc., on abscissa scale in middle of figure). At an opacity of 10 (or density of 1.0 if ordinary ordinate used) the relative intensities of each line, and background if significant, are read off on the intensity scale (see arrows in *B* to indicate method of measurement of intensity). In *A* there is a relatively high concentration of the analysis element (strontium), whereas in *B* its concentration is very much lower. Note that the intensity scale *decreases* from left to right, whereas the sector scale is reversed.

mittency effects are ignored (for practical purposes this may be done), this separation is a measure of the intensity ratio of the two lines. Strock (1936b) describes the method of plotting a working curve and the analysis of unknowns, using the separation of the internal standard line-analysis line characteristic curves as a measure of the intensity ratio of the analysis pair. It may be more convenient to read off (at constant density) the relative intensities of analysis and internal standard lines on the abscissa, as indicated in Fig. 9–8. In this way it is fairly easy to make a correction for background (Section 9–7). Note the disposition of the two abscissa

scales in Fig. 9–8. For plotting the partial characteristic curves (from sector measurements), intensity increases from left to right, whereas a reverse scale is used for evaluating the line intensities.

From a photographic viewpoint, the use of a self-calibrating method ensures the highest accuracy for the measurement of an intensity ratio. However, the improvement in accuracy is usually slight. One disadvantage of self-calibration is that it is somewhat wasteful of plate space.

A deflection ratio method recommended by Twyman (1941) has had considerable application to steel analyses, particularly in England (Barker, 1939). This method has very seldom been employed for the analysis of minerals, rocks, soils, and related materials. Because the method seems worthy of more consideration than it has yet received for the analysis of these substances, it is described here in some detail.

It can be shown (Twyman, 1941, pp. 97–98) that

$$\log \frac{I_s}{I_a} = \frac{1}{\gamma} \log \frac{d_a}{d_s} \qquad (9\text{–}1)$$

holds for the straight-line portion of the characteristic curve of a photographic emulsion. I = intensity and d = galvanometer deflection, while the subscripts s and a refer to internal standard and analysis lines respectively. For most plate emulsions, lines of density greater than about 0.3–0.4 can be used. From Eq. (9–1) it is evident that a working curve may be obtained by plotting log concentration vs $\log \frac{d_a}{d_s}$. The slope of such a curve depends on γ. Fig. 9–9 shows a working curve constructed in this way, using the deflection data (column 1) in Table 9–3. This curve shows a straight line portion over the concentration range 0.45–2.5% K_2O. The appearance of a shoulder at relatively high potash concentrations is due to self-absorption (compare Fig. 9–5) and the deviation from linearity at relatively low concentrations develops when the density of K 4047 is less than about 0.3. The spread of the triplicate points is to be noted. At 0.1% K_2O there is a large spread of points, due to the presence of some background and the low density of K 4047. A considerable spread of points caused by self-absorption of K 4047 at relatively high concentrations is to be observed at 5.0 and 7.5% K_2O (compare Fig. 9–5). Within the usable range in this particular example (0.5–3.0% K_2O), however, the plotted points show little spread and comparing well with those of Fig. 9–5. In this procedure, a separate working curve is drawn for each plate unless darkroom conditions have been very closely controlled. In the latter case one working curve suffices for several unknown plates. The deflection ratio method is rapid and could conveniently be applied to the analysis of minerals, rocks, soils, and related materials. One drawback of this method

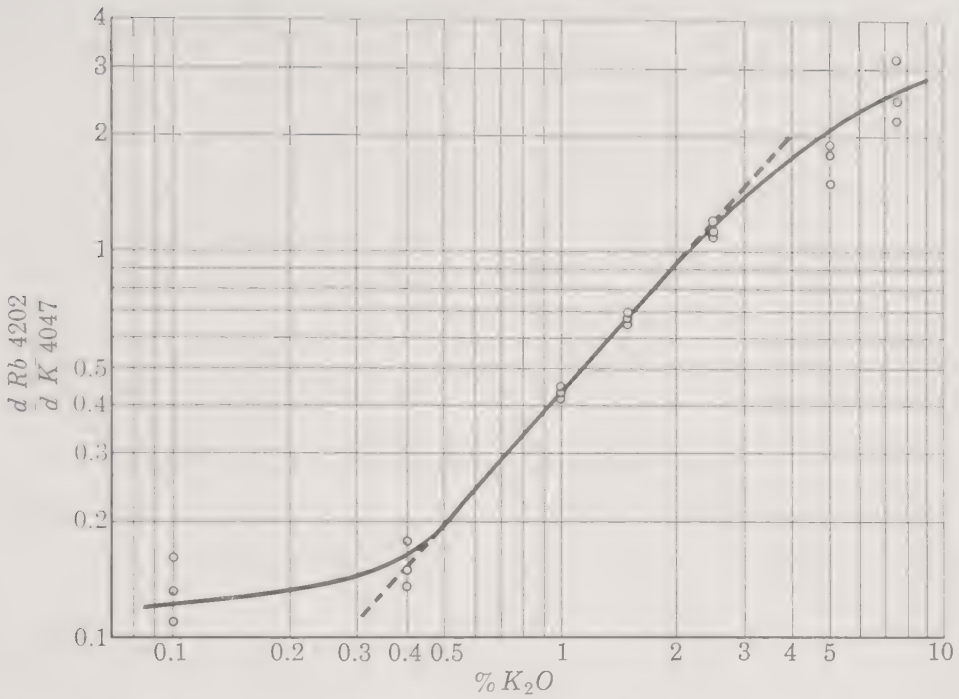

Fig. 9–9. Working curve obtained by plotting the log line deflection ratio of the analysis pair vs log % K_2O. This method is rapid but somewhat restricted; only lines of density which are on the straight line portion of the characteristic curve may be used.

of determining intensity ratios is that a correction cannot be made for background.

Various aids have been described for speeding the conversion of microphotometric data to concentrations. These aids, usually referred to as graphical calculators, are of particular value in routine laboratories where large numbers of specimens have to be analyzed as quickly as possible. Such calculators are of less value in laboratories where most work is of a research nature. A fairly complete bibliography of papers which describe the construction and operation of these calculators may be found in Mitchell (1948, p. 34).

If a microphotometer is not available, line intensities and their ratios can quite frequently be determined with accuracy sufficient for some purposes through the use of the logarithmic sector. The optical requirements are the same as for the step sector (Section 9–3). Because of the smooth cut of the log sector, the resultant lines on the spectrogram taper and fade away into background. Measurements of the lengths of lines are made. If no internal standard is employed, a working curve can be obtained by a plot of line length vs log concentration, whereas if an internal standard is used, the difference in line lengths of internal standard and analysis lines

is plotted vs log concentration. Background correction cannot be made. The log sector is not in frequent use nowadays, but it has a place in laboratories which do not possess a microphotometer. One of the most recent publications to describe the application of the log sector is that of Rankama and Joensuu (1946). A complete bibliography of its use is given there.

9–6. Visual determination of line intensity for semiquantitative analysis. For many purposes, adequate accuracy can be obtained by making a visual comparison of the spectral intensities of the unknowns with those of standard specimens. Intensity estimates can often be made within $\pm 30\%$ of the correct value. A practiced eye is an asset here. If a step sector is employed when the spectra of standards and unknowns are recorded, more accurate intensity comparisons can be made. A variation in background usually introduces a major source of error when relatively weak lines are examined; weak lines on a weak background usually appear stronger than more intense lines on a heavier background.

9–7. Correction for the presence of background. On examining an exposed spectrographic plate, the observer is first aware of the presence of many lines and bands, but a closer scrutiny will frequently reveal some general darkening. This is background. Background is due mainly to the emission of continuous radiation from the electrode tips, incandescent particles within the source column, and scattered radiation within the spectrograph. Much of the continuous radiation from the arc column is due to glowing particles of carbon and metal (the rare earth elements, for example) which have been reduced and which emit continuous radiation on oxidation. Hence by arcing in an atmosphere free from oxygen (in He or A for example) background may be reduced. In small spectrographs, band spectra are not resolved and may be regarded as background. Halation near very strong lines also contributes to background. Some plates are heavily fogged because of poor storage facilities, prolonged exposure to heat, or age, and such so-called "chemical fogging" adds to background.

When a line is located in a region of background, the measured photographic response is due to the intensity of the line plus the intensity of background. Pierce and Nachtrieb (1941) have shown that a correction may therefore be made by subtracting background intensity from total intensity. This may be done on a properly calibrated plate. Microphotometric measurements are made adjacent to the line, but free from its halation. Fig. 9–10 (A) shows the intensity profile of a line located on a background of uniform intensity, whereas Fig. 9–10 (B) shows the presence of a variable background. This condition obtains when the line under consideration is near a strongly halated line. The arrows indicate where microphotometric measurements should be made. When background

varies, its correction is usually not as accurate as in Fig. 9–10 (A), and the mean of two readings, one on each side of the line, should be used. Because background response is usually low, it is more accurately determined with the aid of a plot of density vs intensity (Fig. 9–1).

The method of subtracting background intensity is in common use, and is valid provided the photographic response intensity relationship is the same for monochromatic and continuous radiation. Strock (1936 b) has reported that the slope of the characteristic curve for monochromatic radiation was 1.5 times greater than for continuous radiation. However, Pierce and Nachtrieb (1941) find no such difference for the plates they observed; likewise, Ahrens (1945 d) finds that for Ilford ordinary plates no slope differences are observable. Mitchell (1948) refers to such differences. (See also comments by Oertel, 1947.) Their cause may be due to the presence of an Eberhard effect. Because of this possibility of differences of slope in the characteristic curves for monochromatic and continuous radiation, it may sometimes be wiser to omit background correction if the background is not excessively dense and does not fluctuate unduly. If a heavy background is present and the analyst has several possible analysis and internal standard lines at his disposal, several line pairs should be used. Each pair is used over a limited concentration range of the analysis element for which the relative intensities of both lines are roughly the same. Background will then influence both lines to the same extent and may be ignored. The use of homologous line pairs (Section 7–15) is particularly valuable in this respect.

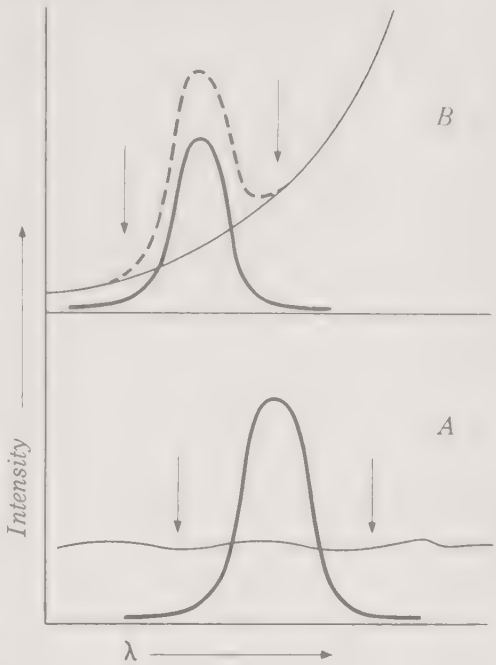

Fig. 9–10. Measurement of background intensity. In *A*, background intensity is relatively uniform and measurements may be taken on either side of the line (see arrows), whereas in *B*, background changes rapidly and measurements should be made on both sides and averaged. *B* may be taken as an example of a line located near a very strong line. The broken curve indicates profile of the line in the presence of interference.

If a self-calibrating method (Section 9–5) has been employed for the determination of intensity ratios, correction may be made as indicated in Fig. 9–8. A partial characteristic curve is drawn for background, and at a density of 1.0 the intensity of background is read off the abscissa. This

value is subtracted from the total intensity. Because background intensity is likely to be low, considerable extrapolation may be necessary to a density of 1.0. If log-scale paper is not available, the use of subtraction logarithms will considerably shorten the time for obtaining the final intensity values (Mitchell 1948, p. 29).

The presence of an over-all background on a plate sometimes poses a serious problem for the analyst. Some operators have recommended that the general background be regarded as "clear glass." Provided general background is weak, no serious error appears to be introduced, but the assumption that galvanometer deflection ("clear glass" deflection) for a heavy background is equivalent to d_0 appears unsatisfactory. Significant errors resulting from such an assumption have been observed. There is little doubt that the most satisfactory results are obtained from clear, clean plates. To ascertain whether intensity measurements can be made accurately on a plate which has a heavy over-all background, relative intensities of different components in a multiplet can be determined and checked against the known values.

For further discussion on background correction, see Strock (1936 b), Kaiser (1948), and Mitchell (1948, pp. 26–33).

It is sometimes found that even after careful attention has been given to background correction the working curve still shows a toe at relatively low concentrations. This is usually due to the presence of a trace of the analysis element as an impurity in the base material. To apply a correction for a base impurity, the intensity of the analysis line is determined in the base material (after correction for background intensity, if necessary) and then subtracted from the line intensities for each standard. If an internal standard has been used, the intensity ratio of the line pair in the base material is subtracted. These intensities and intensity ratios should be estimated accurately (mean of several determinations). Alternatively, the "addition method" of plotting (Section 9–4) may be used to evaluate the concentration of the unknown in the base material.

9–8. Correction for the presence of an interfering line. Sometimes the analyst is confronted with the problem of having either to attempt an analysis using lines which are likely to show some interference, or to discard the analysis completely. Geochemists are particularly loath to "lose elements." Even if the accuracy of a determination is marred by the presence of an interfering line, the information obtained may nevertheless be valuable. The analyst will then attempt to salvage his lines and use them in the most fruitful way.

Fig. 9–11 (A), (B), and (C) show three types of line interference. In (A) the interfering line (light curve) is of the same wavelength as the analysis

line and on the spectrogram a single line is observed. Whether or not a pair of lines of similar wavelength will appear as a single line depends on the dispersion of the spectrograph and also on slit width (see discussion on B). The method that will be described for the correction of interference applies only when interference and analysis lines appear as a single line on the spectrogram.

The assumption here is that the total measured photographic response is produced by the sum of the intensities of analysis and interfering lines. Correction cannot of course be attempted when the intensity of the interference line is excessive. Consider the example of the analysis of indium in mica (Ahrens and Liebenberg, 1950). In 3256.09 was used. In some mica specimens interference from Mn 3256.14 was suspected. Its presence was verified and corrected as follows. A neighboring manganese line (the check line) of the same multiplet and slightly more intense than Mn 3256 was sought. Mn 3248.516 was chosen and the ratio $\frac{I \text{ Mn } 3256}{I \text{ Mn } 3247}$ was estimated as 0.59 in the absence of indium. If Mn 3248 is absent from the spectrum of the specimen analyzed, there will be no interference from Mn 3256 with In 3256; if the check line is present, the corrected intensity of In 3256 is given by subtracting 0.59 $\times$ the intensity of Mn 3248, from the total intensity at λ 3256.

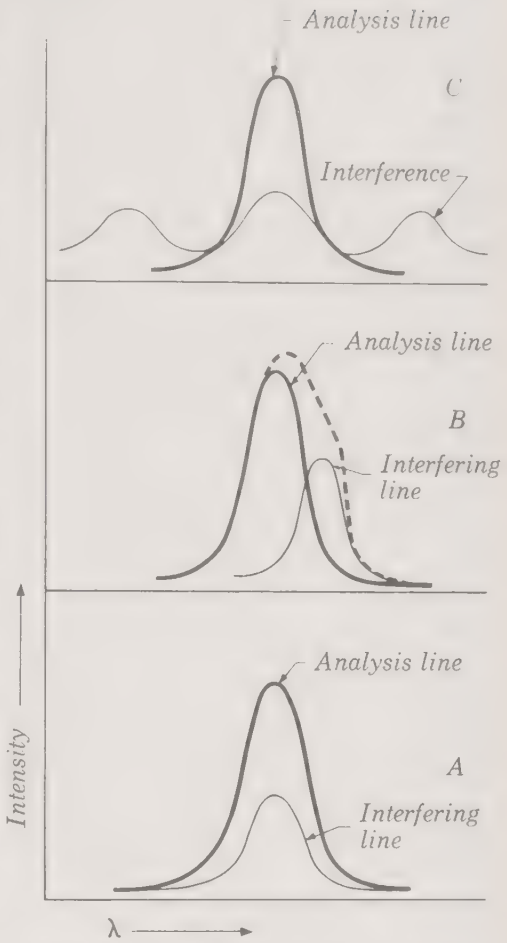

Fig. 9–11. Various types of line interference. In *A*, analysis and interfering lines have the same wavelength; in *B*, there is a slight wavelength difference and the broken curve indicates the profile of the analysis line in the presence of interference. *C* is an example of interference from a band spectrum.

This correction holds most rigorously when interfering and check lines belong to the same multiplet, because then their ratio is always constant. Usually, however, correction is also valid if both lines are arc lines. Correction for interference of Fe 4202.031 with Rb 4201.85 is described in Section 12–2.

In (B) correction is not so easily applied, but if the slit width is increased, it is often possible to obtain a single broad line on the spectrogram. Correction can then be applied as in (A). Because the spectra of minerals, rocks, and soils are often extremely complex, it is frequently impossible to use such a broad slit lest other neighboring lines interfere. (C) shows interference from the resolved components of a band spectrum. Here a correction may sometimes be applied, as in (A). One example (Y 3710) is discussed in Chapter 16.

The bibliography on the photographic measurement of radiant energy is voluminous and for further reading the *Index to the Literature on Spectrochemical Analysis* (Parts 1 and 2) and *Spectrochimica Acta* (Vol. 3) should be consulted.

CHAPTER 10

THE EMISSION OF BAND SPECTRA FROM THE ARC

10–1. Molecular excitation. Certain molecules which can exist in the arc may be excited to emit *band spectra*, also known as *molecular spectra*. All spectrochemists are familiar, for example, with the appearance of the so-called cyanogen bands due to excitation of the molecule CN (Plate 4). The emission of these band spectra may be explained in the same general way as the emission of spectral lines from atoms and ions. The molecule can be energized to certain discrete levels or states in an appropriate source; on its return to its original state, it emits radiation in the form of band spectra. The general appearance of the usual band spectrum differs from that of a line spectrum because of a difference in the types of energy levels involved.

A molecular emitter can exist in three types of energy states. Discrete energy levels are associated with (1) the orbital movement of the electron about the molecule (electronic levels), (2) the vibration of each component atom comprising the molecule (vibrational levels), and (3) the rotation of the molecule as a whole (rotational levels). With each electronic level is associated a suite of vibrational levels, and with each vibrational level is associated a suite of rotational levels. Purely electronic transitions involve the largest energy differences and rotational transitions the smallest. These latter cause the appearance of fine structure in a band spectrum. Plate 4 shows clearly the structure of the CN violet bands. The fine structure is observable only if a large dispersion (obtainable by the use of large grating spectrographs) is used.

The electronic quantum number can assume values of 0, 1, 2, 3, . . . , for which each value is symbolized as Σ, Π, Δ, and Φ respectively. The electronic quantum number of the molecular emitter is to be compared with the orbital quantum number L in line spectra, for which 0 [illegible]arly 3 = S, P, D, and F respectively. The vibrational quantum symbolized as v, can equal 0, 1, 2, 3, . . . v' and v'' refer r[illegible] emission is upper and lower vibrational levels. J is the symbol fo[illegible] outer fringes. quantum number which determines the angular momentu[illegible] spectrochemical Whereas fine structure in atomic spectra can be attributed [illegible] Several elements in band spectra it is due to rotation of the molecule. [illegible]es within CN

Except for a very brief outline of the nature of molecular e[illegible] 4034, 4033, the molecular quantum number notation, no more purely [illegible]5, Nb 4058 aspects will be given here. The theory of the emission of [illegible] desirable to

is discussed in detail by Herzberg (1950) and more briefly by Harrison, Lord, and Loofbourow (1948).

Because the excitation potentials of many molecules fall within the excitation range of the arc, the emission of band spectra from these molecules is to be expected. Excitation potential is, however, not the only factor to consider when attempting to determine which molecules will emit in an arc and which will not. If the heat of dissociation of the molecule is relatively low, such a molecule is likely to dissociate before excitation is possible; a cooler flame provides a more favorable energetic environment for emission from such molecules than do arcs. Further, the nature of the excitation within the source is important. Thus, although the arc has sufficient energy to excite NiH, such emission has not been recorded in a nickel arc in an atmosphere of hydrogen. NiH emission develops, however, in such purely thermal sources as flames and high-temperature furnaces. The probability of NiH excitation is apparently greater in a source where there are collisions with other particles of roughly the same mass, as in the furnace, than in the arc where there are in addition many fast moving electrons. See Gaydon (1947).

Those molecules known to emit spectra from the d.c. arc are given in Table 10–1. A few of them are doubtful emitters, and may be extremely feeble.

Table 10-1

AlO, AsO, BO, BaBr, BaCl, BaF, BaO, BeF, BiO, C_2, CN, CaBr, CaCl, CaO, CaF, CuO, FeO, GdO, GeO_2, HfO, InO, LaO, LuO, MgBr, MgCl, MgF, MgO, MnO, NiO, PO, PbO, PrO, S_2 (?), SO, SiO, SbO, ScO, SrCl, SrF, SrI(?), SrO, TiO, YO, and ZrO.

Most of this information has been obtained from Pearse and Gaydon (1941)

Some of these molecular emitters are oxides of the commoner elements
in minerals and rocks and may cause considerable interference; these
th CN will be discussed in some detail. Occasionally, molecular
e employed for the identification of elements. Fluorine is
ts detection and estimation are discussed in Chapter 13.

...s of some of the commoner molecular emitters.

systems of bands, referred to as cyanogen red (excitation
volts) and cyanogen violet (excitation potential 3.2 volts), are
N from a carbon arc source. The violet system is much more
he red and is the usual one observed in analysis. There are

three main sequences in the violet system, the heads of which are at 3590, 3883, and 4216 A respectively. Table 10–2 gives the wavelengths of the vibrational components in each band sequence. Wavelengths of fine structure (rotational) components are not included. The wavelengths and approximate intensities given are from Pearse and Gaydon (1941). Intensities are based on a 1–10 scale.

Table 10-2 CN bands

	λ	I	v	v	
	4606.1	1	0	2	Weak bands
	4578.0	2	1	3	
	4553.1	2	2	4	
	4531.9	2	3	5	
	4514.8	2	4	6	
	4502.2	2	5	7	
Head	4216.0	9	0	1	Three main sequences of the cyanogen violet system
	4197.2	8	1	2	
	4181.0	7	2	3	
	4167.8	6	3	4	
	4158.1	5	4	5	
	4152.4	4	5	6	
Head	3883.4	10	0	0	
	3871.4	9	1	1	
	3861.9	8	2	2	
	3854.7	6	3	3	
Head	3590.4	8	1	0	
	3585.9	7	2	1	
	3583.9	6	3	2	

The fine structure of the CN bands is either unresolved or poorly resolved under relatively small dispersion (Plate 4a), but under high dispersion (as obtained in a large grating spectrograph) this structure is very clearly shown (Plate 4b).

A high temperature in the arc favors CN emission. Peak emission is at the hot core of the arc and falls away sharply at the outer fringes. Because carbon (or graphite) electrodes are usually used in spectrochemical analysis, CN emission is always present to some degree. Several elements have some sensitive lines and a few their most sensitive lines within CN bands. Examples of these lines are Ga 4172, Pb 4057, Mn 4034, 4033, and 4030, K 4044 and 4047, Rb 4202, Sr 4077 and 4215, Tl 3775, Nb 4058 and 4079, Mo 3864 and 3798, and others. It is therefore desirable to

quench CN emission as effectively as possible if any of these lines are to be used.

One of three methods may be used to reduce CN emission. First, the arc may be made to burn in a nitrogen-free atmosphere; second, special precautions may be taken to ensure that only a trace of electrode carbon enters the arc column; and third, a substance other than carbon may be used for the electrodes.

Steadman (1943) used an atmosphere of CO_2 to clear the CN bands. Smith and Wiggins (1948) and Wiggins (1949) employed steam; their apparatus seems very simple and easy to operate. Marks and Gardner (1947) describe a chamber in which arcs may be operated in any desired atmosphere. Ashton (1939) has also discussed the suppression of CN emission. Johnson and Norman (1943) have employed CO_2 to suppress air bands. Use may also be made of the noble gases He and A to clear CN emission.

Even for the carbon arc in an air atmosphere, it is sometimes possible to quench CN so effectively that several of the sensitive lines of elements located within CN bands can be used. For this purpose the presence of an alkali metal salt is recommended. Such salts aid in suppressing CN emission for several reasons. First, the arc strikes the sample and does not wander over the crater walls and thereby consume large quantities of carbon; second, less carbon is likely to distill from the electrode tips because of the cooling effect of the alkali metal; and third, because of the prevailing low temperature within the arc column in the presence of alkali metals only a relatively small proportion of the carbon that does enter the arc column is excited as CN. As the alkali metals are usually volatile, however, CN emission is only really cleared during the first period of arcing. Therefore, the exposure must be stopped when the main bulk of the alkali metals has distilled. This point can usually be determined by an inspection of the arc. As soon as the alkali metals have vaporized, the arc loses its flame-like appearance. Observations on a voltmeter which records gap voltage will also quickly show when the alkali metals have volatilized; the signal is a sudden increase in voltage. During the first arcing period, other relatively volatile elements (for example, Pb, Ga, and Tl) will distill with the alkali metals. As a result, Pb 4057, Ga 4172, Rb 4202, K 4044 and 4047, and Tl 3775 may be successfully employed. A good example of how each of these lines may be recorded on a spectrum almost completely free from CN emission is furnished by arcing a specimen of *feldspar* (preferably a hydrothermal type such as *amazonite*) for about one minute at 3–6 amp, using anode excitation.

If cathode layer excitation is used, CN emission cannot be controlled so effectively. Much more carbon enters the arc colmun and it becomes

impossible to obtain a really cool arc temperature because the concentration of alkali metal in the arc column is low.

On some occasions CN emission can be quenched throughout the exposure time, provided all elements are made relatively volatile. Thus on treatment with hydrofluoric acid, silicates are attacked and fluorides which may be dried and arced are obtained (Ahrens, 1949). Ahrens (1947) shows the spectrum of a fluoride residue of the rare cesium silicate, *pollucite*. CN background is virtually absent because of a high concentration of alkali metal throughout the arcing period. The lines K 4044–4047, Rb 4202, Ga 4172, Tl 3775, and Sr 4077 are clearly evident. Strontium is relatively involatile, however, and by using Sr 4077 strontium cannot normally be detected in pollucite because of intense CN emission during the later arcing period (see also Fig. 13–1). The presence of Sr 4077 in this example is of unusual interest; it has been emitted by a trace of strontium, the daughter by β-decay of rubidium, two lines of which (Rb 4202 and 4215) are also evident.

Table 10-3 AlO bands

λ	I	v'	v"
5424.3	2	5	7
5410.5	3	4	6
5394.8	3	3	5
5377.4	2	2	4
5358.1	2	1	3
5336.9	1	0	2
5160.8	3	4	5
5142.9	4	3	4
5123.3	5	2	3
5102.1	5	1	2
5079.3	4	0	1
4888.4	6	2	2
4866.1	9	1	1
4842.1	10	0	0
4735.5	6	5	4
4715.5	6	4	3
4694.6	7	3	2
4672.0	8	2	1
4648.2	8	1	0
4557.5	3	6	4
4537.6	4	5	3
4516.3	4	4	2
4494.0	3	3	1
4470.5	2	2	0
4393.8	1	7	4
4373.7	1	6	3

Because of the disturbance caused by CN emission, copper has quite often been used for electrode material.

AlO Unlike the CN bands, these are degraded toward the red. They are readily observed when an aluminum mineral or rock is arced and can cause considerable interference, particularly in the wavelength range 4350–4900 A. Some of the sensitive vanadium lines of the group at 4390 A sometimes suffer interference. AlO bands develop in a relatively cool temperature, and the optimum temperature for their emission is approximately 3000–4000°A; consequently this emission is mainly from the fringe of the arc. AlO bands may be readily observed by arcing a granite specimen + 5% KCl, at a low amperage. The same specimen mixed with carbon powder and arced at a relatively high amperage (8 amp) shows very poor development of these bands.

AlO bands show a well-marked rotational fine structure. Wavelength and intensity measurements (after Pearse and Gaydon, 1941) for vibrational components are given in Table 10–3.

CaO Bands due to CaO are particularly evident when calcium-rich substances are arced. These bands are very diffuse and, unlike those of AlO and CN, lack rotational fine structure. There are two main groups: the orange system at 5983–6362 A, and a green system at 5473–5560 A.

SiO SiO bands are emitted when silicates are arced. Emission is particularly intense from quartz, sand, and any form of silica. Porlezza (1924) has referred to interference from SiO bands. Where such interference is encountered, Porlezza suggests the removal of silicon from the specimen prior to analysis. Ahrens (1943 b) attempted to determine wolfram in siliceous tailings in an ore dressing laboratory by using W 2656 and W 2657 and reported interference from the SiO band with head at 2568 A. Ahrens and Liebenberg (1946) found SiO bands troublesome for

Table 10-4 SiO bands

λ	I	v'	v"
2925.3	2	4	10
2898.4	2	3	9
2871.6	2	2	8
2806.3	2	3	8
2780.5	3	2	7
2755.0	3	1	6
2693.7	5	2	6
2669.0	4	1	5
2587.1	7	1	4
2563.8	8	0	3
2486.8	10	0	2
2413.8	10	0	1

the detection of gold in Witwatersrand "banket" (a siliceous conglomerate). In particular the band with head at 2413 A interfered with the most sensitive gold line, Au 2428. In Section 18–2 the elimination of such interference is discussed. Cooper (1949) also mentions the troublesome presence of SiO bands in some of the specimens he has analyzed. Tank nitrogen was used to eliminate oxygen from the arc and thus quench SiO emission.

In Table 10–4 wavelength measurements for the most intense vibrational heads (Jevons, 1924) are given. Intensity data are from the author's plates.

PART II

THE ELEMENTS

CHAPTER 11

GENERAL SEMIQUANTITATIVE AND QUANTITATIVE METHODS APPLICABLE TO A LARGE NUMBER OF ELEMENTS

Several general methods which handle a relatively large number of elements and which are often applicable to a wide variety of materials have been described. These methods often tend to be semiquantitative, but are frequently valuable because their use enables the analyst to obtain much information about many elements in a short time. For the sake of convenience, all of these methods are described in this chapter.

A semiquantitative method of analysis intended for use on a very wide variety of materials is described by Harvey (1947). Weighed amounts of sample are completely volatilized and selected line-to-background ratios are determined on a microphotometer. Such ratios are assumed to be reasonably constant for a given matrix. If data given in Harvey's publication are used on each matrix, it is claimed that quantitative determinations to within ± 30–50% of the element sought are often possible. The background continuum is used in principle as an internal standard, and conditions of arcing must therefore be closely controlled. The method has been applied to the analysis of Ag, Al, As, Au, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, Ge, Hg, In, K, Li, Mg, Mn, Mo, Na, Nb, Ni, P, Pb, Pd, Pt, Ru, Sb, Si, Sn, Sr, Ta, Te, Ti, Tl, V, W, Zn, and Zr. Anode excitation is used and the sample is loaded into an electrode cavity similar to type 5 in Fig. 5–2. Harvey's method has been used and modified by Addink (1948).

Van Tongeren (1938) has made extensive use of a semiquantitative method for a study of the distribution of several elements in numerous mineral and rock types from the East Indies. Cathode layer excitation was used on a 9 ± 1 mg specimen, which after dilution with Na_2CO_3 was loaded into a cathode 5 mm (ext. diam.) $\times$ 1.1 mm (int. diam.) $\times$ 4 mm (depth). Successive exposures were made on the sample as follows: 30 seconds (2–3 amps); 30 seconds (5 amp); 30 seconds (7 amp); and four 30-second exposures at 9 amp.

The method was employed mainly for the analysis of Sr, Ba, Sc, Y, La, Ce, Nd, Ti, Zr, V, Cr, Mn, Ni, Co, Ga, and Pb. Van Tongeren records many observations on the behavior of these elements in the arc, as well as of other elements which, however, were not detectable in the unknowns. Semiquantitative determinations were made visually by comparing line responses of the unknowns with those of standards which had been prepared in a base of quartz powder and Na_2CO_3.

Another general method which employs cathode layer excitation is that described by Mitchell (1948). This method has been widely applied to the analysis of plant ash, soils, minerals, and rocks. About 7–8 mg of specimen is mixed 1:1 with carbon powder and loaded into a cathode cavity 2.8 mm (ext. diam.) × 0.8 (int. diam.) × 8 mm (depth). This is arced at 9 amp; three successive exposures of about one minute are made. To facilitate visual comparison of line response, a step sector is employed and the plates are examined in a comparator. Most determinations fall within about ±30–40% of the amount present.

Mitchell used a very complex base for the preparation of standards, particularly for the analysis of soils. Its composition is as follows: 63% SiO_2, 20% Al_2O_3, 5% Fe_2O_3, 2% CaO, 2% MgO, 3.5% Na_2CO_3, 3.5% K_2SO_4, and 1% TiO_2. The mixture is sintered overnight at 1250°C. Because the constituents of this base are so numerous, risk of contamination is considerable and especial attention must be given to the purity of each ingredient. Mitchell gives details (p. 128) on methods for the preparation of each ingredient in a very pure form.

Many of the methods used by Goldschmidt and co-workers at Göttingen during the years 1931–36 were semiquantitative and similar in several respects to the procedures of Van Torgeren and Mitchell. Some of these methods are referred to in later chapters. Several publications by Marks and co-workers describe the use of a general method which has been applied to the analysis of various elements in ores. The procedure for Ge, Sn, and Pb is described by Marks and Hall (1946); for Be, Cd, Zn, and In by Marks and Jones (1948); for Ag, by Marks and Potter (1948); and for Tl, by Marks and Potter (1949). The method is one of "total energy" (Section 7–18), and very small, accurately weighed quantities (usually 0.4–4.0 mg) of specimen are completely volatilized after addition of a lime:graphite mixture. The presence of $CaCO_3$ serves as a buffer, and has been found effective in nearly all matrices. One example of the efficacy of buffering by $CaCO_3$ is given in Section 8–3. $BaCO_3$ is sometimes used instead (Section 15–3). The quantity of the sample weighed depends on the concentration of the unknown. 4-amp anode excitation is used, and a step spectrum from a Pfund iron arc is employed as a reference spectrum. The results thus far published are very encouraging, and the general procedure appears to have wide application to *ore* analysis. Accuracy appears adequate for many purposes, particularly for quick scanning of deposits. Table 11–1 shows some typical analytical data which should provide a good indication of reproducibility. Each specimen has been analyzed four or more times. (a), (b), (c), and (d) refer to different specimens.

The silver determinations are most highly reproducible, whereas those

Table 11-1

% Tin (Marks and Hall, 1946)

(a)	(b)	(c)	(d)
0.025	0.097	0.19	0.60
0.026	0.088	0.13	0.64
0.028	0.097	0.26	0.70
0.027	0.083	0.16	0.45
Av. 0.027	Av. 0.091	Av. 0.18	Av. 0.60

% Lead (Marks and Hall, 1946)

(a)	(b)	(c)	(d)
0.22	0.42	1.17	4.01
0.35	0.76	1.03	3.84
0.26	0.55	1.26	3.45
0.29	0.31	1.11	4.32
0.34			
0.30	Av. 0.51	Av. 1.14	Av. 3.90
Av. 0.28			

% Germanium (Marks and Hall, 1946)

(a)	(b)
0.011	0.038
0.015	0.039
0.013	0.035
0.017	0.037
Av. 0.014	Av. 0.037

% Silver (Marks and Potter, 1948)

0.0051	0.019	0.043	0.186
0.0053	0.018	0.042	0.196
0.0057	0.022	0.043	0.193
0.0063	0.020	0.040	0.158
Av. 0.0056	Av. 0.020	Av. 0.040	Av. 0.183

of lead are poorest. Other information of this type on Cd, Zn, In, and Tl may be found in the publications of Marks and co-workers. In general, reproducibility is of the same magnitude as for the examples given here.

Thus far no general methods which employ internal standardization have been discussed. If a high degree of accuracy is sought, it is often unwise to attempt the use of one internal standard for the analysis of many elements whose properties differ considerably in the arc. Each element, or a limited number of elements, may require a separate internal

standard, and a complete and accurate analysis becomes very tedious. At the Cabot Spectrographic Laboratory, M. I. T., attempts are being made to develop methods which combine the rapidity of the typically semiquantitative methods with the accuracy of the truly quantitative methods. These procedures are intended for general application to silicate minerals and rocks and also to soils. Two internal standards are used, one for each of two groups of elements. Volatility is considered the most important of the properties which determine the efficacy of an element as an internal standard. Consequently all elements sought are grouped into so-called volatile and involatile groups. Indium (added as In_2O_3) is the internal standard for the volatile group of elements, namely, Pb, Ga, Cu, Ag, Zn, and Ge. Low-amperage anode excitation (3–4 amp) is employed and the first four minutes of arcing are recorded. The anode shape is the same as type 3 in Fig. 5–4.

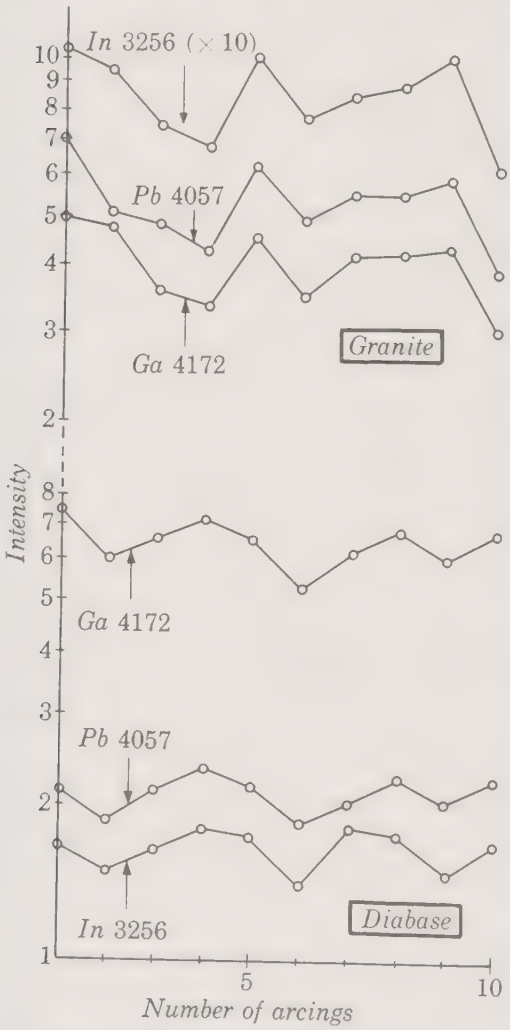

Fig. 11–1. From this plot of intensity vs number of arcings it may be seen that the intensity fluctuation of the internal standard line (In 3256) is in reasonable sympathy with the intensity fluctuations of the analysis lines (Pb 4057 and Ga 4172).

Although the investigations are not yet completed, the efficacy of indium as an internal standard for Ga, Cu, and Pb in rocks has been found satisfactory. Its use is demonstrated in Fig. 11–1. One specimen of diabase and one of granite were arced ten times. The figure shows plots of line intensity (log scale) vs number of arcings for Pb 4057, Ga 4172, Cu 3274, and In 3256. (Ordinarily In 4101 is better placed than In 3256 for Pb 4057 and Ga 4172, but in these examples In 4101 was excessively strong and In 3256 has been used in its stead.) It is quite clear that the intensity changes of the internal standard line compensate reasonably well for the fluctuations of the intensities of the analysis lines. Some of the intensities have been multiplied by a

Table 11-2

	Granite			Diabase		
	$\%Ga_2O_3$	%PbO	%CuO	$\%Ga_2O_3$	%PbO	%CuO
	0.0026	0.0036	0.00042	0.0027	0.00080	0.0060
	-	0.0026	0.00090	0.0027	0.00076	0.0054
	0.0026	0.0028	0.00054	0.0028	0.00080	0.0054
	0.0026	0.0027	0.00064	0.0031	0.00078	0.0054
	-	0.0028	0.00068	0.0028	0.00077	0.0058
	0.0024	0.0027	0.00046	0.0025	0.00076	0.0052
	0.0025	0.0030	0.00056	0.0028	0.00070	0.0048
	0.0026	0.0029	0.00066	0.0027	0.00082	0.0059
	0.0027	0.0026	0.00052	0.0023	0.00082	0.0052
	0.0024	0.0026	0.00062	0.0025	0.00082	0.0050
Mean	0.0026	0.0028	0.00062	0.0026	0.00078	0.0055
Standard deviation	±5%	±11%	±30%*	±8%	±5%	±6%

*The standard deviation for copper in the granite specimen is high because the copper content is very low and the analysis line is faint and not accurately measurable.

constant factor for convenience in plotting. Table 11–2 gives the actual percentages found for each determination, together with a statement of the approximate standard deviation.

For the analysis of relatively involatile elements (Be, Ba, Sr, V, Cr, Ni, Co, Mo, Sc, Y, La, Nd, Zr) in rocks, common rock-forming minerals, and soils, the use of palladium as an internal standard is being investigated. Bray (1942), who employed cathode layer excitation, used palladium (as the chloride) as an internal standard for the analysis of Sc, La, Ce, Nd, Zr, V, Cr, Co, Ni, Pb, and Zn. No reproducibility data are given. Because of the relatively high volatility of zinc and lead, however, it would seem that palladium does not offer as satisfactory an internal standardization for these two elements as it does for the others.

In the Cabot Spectrographic Laboratory, each specimen is mixed with two parts of carbon and is arced to completion at 8 amp, using anode excitation and a carbon anode shape similar to that of type 3 in Fig. 5–4. The investigation has not been completed, but reproducibility data on Sc, Zr, and Co in the diabase and granite specimens already referred to are given in Table 11–3. A statement of the approximate standard deviation is also given. The composition of the synthetic base which has been used for the analysis of the volatile and involatile elements is as follows: 25% Al_2O_3, 60% SiO_2, and 15% Na_2CO_3. Before use, sinter overnight at 900–1000°C.

Table 11-3

	Granite		Diabase	
	$\%Sc_2O_3$	$\%ZrO_2$	$\%ZrO_2$	%CoO
	0.00068	0.042	0.014	0.0038
	0.00056	0.041	0.014	0.0042
	0.00061	0.040	0.013	0.0040
	0.00060	0.040	0.014	0.0038
	0.00057	0.037	0.012	0.0032
	0.00055	0.038	0.014	0.0039
	0.00068	0.039	0.014	0.0036
	0.00053	0.039	0.013	0.0039
	0.00060	0.040	0.013	0.0030
	0.00063	0.038	0.012	0.0040
Mean	0.00060	0.039	0.013	0.0038
Standard deviation	±8%	±4%	±8%	±11%

Mitchell (1948, p. 87) describes a quantitative method which has been developed for the determination of various minor constituents in soil extract, plant ash, and soil at the Macaulay Institute for Soil Research, Aberdeen. Iron is used as a variable internal standard (Section 7–4) and should be present at a concentration within 2–20% Fe_2O_3. In the concentration procedure which is used, a mixture of 8-hydroxyquinoline, tannic acid, and thionalide (Mitchell and Scott, 1947) precipitates Co, Ni, Mo, Cr, V, Be, Ge, Sn, Pb, Ti, Zn, and Cd and probably Ga, Tl, and Ag as well. The quinolates of aluminum and iron act as a carrier precipitate and the trace constituents are concentrated by a factor of 500–1000. If the original specimen is poor in aluminum, this element is added in appropriate amount (Mitchell, 1948, p. 122). The alumina-rich precipitate is ashed at about 450°C in a muffle furnace. It is then arced, using cathode layer excitation and a 9-amp arc. An alumina base is used for the preparation of standards. One advantage of this general procedure is that the possible influence of a variation of composition on line intensity is removed because determinations are always carried out in an alumina matrix.

The concentration of the variable internal standard must be known and may be determined as described by Mitchell (1948, pp. 127–128). The method of obtaining a working curve for the determination of the unknowns when using this variable internal standard procedure is described by Mitchell (1948, pp. 22–26).

Various iron lines are used as internal standard lines. For the analysis of zinc in particular, and to a lesser extent for the analysis of other volatile

elements, the use of iron has been found unsatisfactory because of large differences in volatilization rates. Cadmium has been added and used as an internal standard for zinc.

Although this general concentration method has not been applied to minerals and rocks, such an application could undoubtedly be made.

Some of the methods referred to in Chapter 23 (major constituents) are general. There is often no sharp division between a so-called general procedure and one designed for the analysis of one or a very limited number of elements, and the distinction made here is arbitrary.

CHAPTER 12

Li; Rb AND Cs

12–1. Lithium. Of the three rare alkali metals, Li, Rb, and Cs, lithium is most commonly reported in the spectrochemical analysis of minerals and rocks. This is not really surprising, because although lithium is somewhat rarer than rubidium (the commonest rare alkali metal), it has a high spectral sensitivity and is extremely widespread. Because the radius of Li^+ (0.68A) is significantly smaller than the radii of the other alkali metals, Li^+ enters mineral structures octahedrally (6-fold coordination), whereas the others are accommodated in minerals in 8-fold (or greater) coordination. As a result, lithium cannot be regarded as geochemically associated with the other alkali metals. With the exception of *quartz* and *feldspar*, nearly all common silicate minerals contain octahedral structure sites. Lithium has been detected in almost all ferromagnesian minerals and the *micas*, but very rarely in *feldspar*. Li^+ is the only monovalent cation which can enter mineral structures octahedrally. Therefore, in competition with other ions of like size but higher charge (for example, $Mg^{++}$and Fe^{++}), it tends to be rejected in early crystal fractionates and enriches characteristically in minerals which crystallize from late residual pegmatitic emanations such as *muscovite*, *biotite*, and of course the proper lithium minerals.

Many of the main geochemical features of lithium were established by Strock (1936 a), who employed the spectrograph for this purpose. With cathode layer excitation and the use of the lithium resonance line (Li 6707) a detection limit of 0.0001% was attainable. Because of the self-absorptive tendency of this line it was employed only for very low lithium concentrations; for higher concentrations Li 6103 was used (Section 7–16). Strontium (added as $SrCO_3$) was used as the internal standard and the analysis pairs were Li 6707:Sr 6708 and Li 6103:Sr 6708. It was observed that the greatest sensitivity for lithium was obtained in the presence of added NaCl. Thus a specimen of limestone arced as such showed no trace of Li 6707, but after 1:1 dilution with NaCl this line was clearly in evidence. Consequently NaCl was incorporated into the base and was added to each of the unknowns (45% to each). NaCl also provided buffering, but in the presence of large amounts of $CaCO_3$ the buffer action failed, and the intensity of Li 6707 relative to Sr 6708 decreased. This is one of the few examples of ineffective buffer action by an alkali metal. The influence of $CaCO_3$ would probably have been considerably less had either KCl or RbCl been used in place of NaCl.

When one alkali metal is being sought, the presence of one of the others in appreciable amount will invariably improve sensitivity. In this respect the addition of the chloride is usually most effective. All alkali metals are relatively volatile and of about the same volatility.

Sometimes, when a general analysis of a specimen is attempted for several elements, only one exposure is made over a given wavelength range that includes the highest proportion of sensitive lines. Such a wavelength range is not likely to include Li 6707 and Li 6103, and either Li 4603 or Li 3232 may then be used. Although these lines are not as sensitive as Li 6707, they have sufficient sensitivity for the analysis of lithium in many rocks, minerals, and soils.

Wager and Mitchell (1943) and Nockolds and Mitchell (1948) have used Li 3232 for the analysis of lithium in many specimen types. Cathode layer excitation was employed and the limit of detection was 0.001%. If this line is used, a spectrograph of relatively large dispersion must be employed because many common rocks, minerals, and soils emit Ti 3232.28 and Fe 3233.054, which would otherwise interfere with Li 3232.61.

Li 4603 has been used by Ahrens and Liebenberg (1945) for the analysis of lithium in *mica* (see Ahrens, 1945 b). Low amperage anode excitation was employed and a limit of detection of about 0.001–0.005% was attained. Li 4603.00 must be used with caution, however, because of possible interference from Fe 4602.944. This line of iron is quite intense and is apparent in most rock and soil spectra. Because lithium is more volatile than iron, interference is reduced by recording only the early period of arcing. The use of a low amperage is also helpful.

The Foote Mineral Company of Philadelphia has recently reported a spectrochemical procedure developed by Chandler (1949) which is used for the analysis of lithium as a major constituent in lithium source minerals. The specimen is first fused with $KHSO_4$ and then arced, using anode excitation. Potassium is the internal standard and Li 3232:K 3447 the analysis pair. To compete with the chemical analysis of lithium as a major constituent, the highest possible precision must be attained. For this purpose, the choice of potassium has been a logical one, as all the alkali metals have very similar properties. Chandler mentions the use of a rapidly rotating magnet to steady the arc. According to the published results, the spectrochemical accuracy compares favorably with the chemical. An advantage of the spectrochemical procedure in a commercial laboratory is its speed — after receipt of the lithium ore, the analysis is announced within 2–3 hours.

Additional references: Hukuda (1927), Snesarev (1935), Iwamura (1938 b), Tolmachev and Filippov (1936), Patterson (1945), Sahama (1945 a and b), Oplinger (1947), Helz (1945), Tolmachev (1934), Gatterer and Junkes (1940).

12–2. Rubidium and cesium. Rb^+ and Cs^+ are the two largest cations (radii, 1.49 and 1.67 A respectively), and because of their size they are found almost exclusively in potassium minerals, where they are able to replace K^+ (radius 1.33 A). Sodium minerals admit Rb^+ and Cs^+ to a very slight extent because of the great discrepancy between the radius of Na^+ (0.98 A) and those of Rb^+ and Cs^+. In most specimens of *soda feldspar*, for example, the maximum concentration of rubidium is about 0.005% and the approximate limit of detection for this element is 0.001%. As cesium is considerably less abundant and spectrally less sensitive (limit of detection about 0.01%), it is never detectable in sodium minerals. Even in some potassium minerals, cesium may be below its limit of detection. In others, however, notably the potassium minerals of late formation in pegmatites, such as hydrothermal *microcline*, *lepidolite*, *muscovite*, and *biotite*, cesium and rubidium are readily detectable. Here the enrichment is due to the larger size of Cs^+ and Rb^+ relative to K^+. When in competition with K^+, Rb^+ and Cs^+ tend to be rejected from the crystals of relatively early formation and concentrate in the mother liquor fraction. Rubidium is readily detectable in potash rich soils and sedimentary rocks.

Many rock types comparatively rich in potassium contain detectable amounts of rubidium and occasionally cesium. In all instances where the highest sensitivity is desired, the red lines (Rb 7947 and 7800; Cs 8943 and 8543) must be employed. Because of their long wavelengths, red sensitive plates are required, for example, Eastman N or L plates.

These red lines were used by Goldschmidt, Bauer, and Witte (1934), who investigated the geochemistry of rubidium and cesium. Cathode layer excitation was employed. For the preparation of standards, a rubidium glass and *pollucite* (a cesium silicate mineral) were employed for rubidium and cesium respectively, and were diluted with *albite* free from detectable amounts of these two elements. This is an example of the use of as high a proportion as possible of naturally occurring silicates for the preparation of standards, so as to remove possible errors from compositional differences. Ba 7911, 7905, and 7780 were used as internal standard lines for the analysis of rubidium; no internal standardization was attempted for cesium. Unknowns and standards were diluted 1:1 with NaCl so as to buffer against compositional changes and produce a relatively low-temperature arc favorable for the emission of the low-level lines of rubidium and cesium.

Sometimes the wavelength range used will not include the red lines of rubidium and cesium, and the use of other less sensitive lines must then be attempted. In an earlier publication on rubidium and cesium by Goldschmidt, Berman, Hauptmann, and Peters (1933), Rb 4201.85 and Cs 4555.355 were used. Because of the possible interference of Fe 4202.031 and Mn 4201.757 with Rb 4202, and Ti 4555.489 with Cs 4555, a con-

centrate of sulphates free from the presence of the interfering elements was prepared and this was arced.

Ahrens (1945 b), who employed low amperage anode excitation, also used Rb 4202. In *feldspar* no interference from Fe 4202 was evident. In *muscovite* and *biotite* such interference was noted, and corrected in accordance with the procedure described in Section 9–8. Here Fe 4143.871 is the check line. It is a little more intense than Fe 4202.031 and if it is absent there is no interference from Fe 4202. If it is present, the intensity of Fe 4202 is given by 0.85 × the intensity of Fe 4143, and this is subtracted from the intensity of $\left\{ \begin{matrix} \text{Fe} \\ \text{Rb} \end{matrix} \right.$ 4202. Such a correction was considered valid because quartz optics were employed and $\left\{ \begin{matrix} \text{Fe} \\ \text{Rb} \end{matrix} \right.$ 4202 appeared on the spectrogram as a single sharp line. Fe 4143 does not have the same multiplet assignment as Fe 4202 and is thus not an ideal check line (Section 9–8). However, the respective excitation potentials of these two iron lines are almost identical (Ex. pot. 4143 = 4.53 volts; 4202 = 4.42 volts), and the intensity ratio $\frac{4143}{4202}$ should remain constant even if conditions of excitation change considerably. The use of a low amperage is helpful in keeping interference down. Because rubidium is considerably more volatile than iron, the degree of interference is often reasonably low if only the early period of arcing is recorded. In most *rocks*, however, such interference may be so excessive as to make analysis impossible.

CN emission may cause interference, but can be quenched effectively in accordance with the instructions given in Section 10–2. Bertrand (1947) has used Rb 4202 and recommends the use of horizontal electrodes enclosed in a small furnace made from refractory earth to eliminate interference from CN emission.

When the dispersion of the spectrograph is large (2.5–4.0 A/mm), Rb 4201.85 and Fe 4202.031 are resolved. Provided masking from Fe 4202 is not excessive, Rb 4202 can be used. Here again a low amperage arc is used to minimize masking by Fe 4202. In the Cabot Spectrographic Laboratory, several rubidium determinations in granite have been made with Rb 4202, using a spectrograph of large dispersion (2.5 A/mm).

Rubidium does not form any so-called rubidium minerals. A maximum enrichment is reached in *lepidolite* mica, where the concentration averages about 1.5%; these minerals may therefore be used as sources for rubidium. Because of its high rubidium concentration, lepidolite is also used for the determination of geological age by the strontium method (Ahrens, 1949). An accurate analysis may be made of rubidium in lepidolite, using potassium

as an internal standard. The assumption is made that the potassium content is constant. This assumption is not exact, but is valid for many specimens because the potassium concentration varies only slightly. Excellent reproducibility has been found (Standard deviation $\pm 2.7\%$). Each lepidolite specimen is diluted $9\times$ with *albite* (National Bureau of Standards; contains 0.42% K_2O) and is then arced at 3 amp for 5 minutes, using anode excitation. A sector is employed to reduce line intensity by $\frac{7}{8}$. The rubidium content of one lepidolite specimen is carefully determined, using the addition method (Section 9–4). By using this specimen of known rubidium content with those containing known amounts of added rubidium, a working curve may be prepared. Alternatively, a single point working curve may be used because the rubidium concentration varies little (Section 9–4). The analysis pair is Rb 4202 and K 4047. Should the analyst want to safeguard himself against possible significant variation of the potassium content, the addition method procedure may be used for *each* unknown.

Some reproducibility data of four specimens of lepidolite are given in Table 12–1. These data give a good indication of the high reproducibility of the method. The standard deviation of $\pm 2.7\%$ could undoubtedly be slightly improved upon by using a wide slit and a method of self-calibration (Section 9–5).

Cs 4555 may sometimes be used to detect and estimate cesium provided there is no interference from Ti 4555. In *lepidolite* and hydrothermal *microcline* Cs 4555 can be safely used, but in *biotite* there is likely to be interference. In granite-like rocks and potassium-rich soils, emission from

Table 12-1

Locality	Analysis No.	%Rb	Locality	Analysis No.	%Rb
Varutrask, Sweden	1	2.09	Winnipeg River, S.E. Manitoba, Canada	1	2.56
	2	2.12		2	2.56
	3	2.13		3	2.60
	4	2.22		4	2.78
	5	2.14		5	2.65
	Mean	2.14		Mean	2.64
Black Hills, South Dakota	1	1.56	Nomaqualand, South Africa	1	1.26
	2	1.58		2	1.24
	3	1.53		3	1.34
	4	1.56		4	1.29
	5	1.47		5	1.21
	Mean	1.54		Mean	1.25

Cs 4555 is very feeble. Even if there is a photographic response, it is invariably swamped by the emission of Ti 4555, which is relatively intense in these materials.

Cs 4593 is less sensitive than Cs 4555 (by a factor of a little more than two), but danger from interference is low unless quartz prism optics are used. Cs 4593 has been used by Harada (1943) for the analysis of cesium in sea water by cathode layer excitation. Using Cs 4593, cesium would normally be undetectable in the dried salt from sea water, but a chemical concentration was effected with the aid of sodium chlorate ($NaClO_4$) and sodium cobaltinitrite ($Na_3Co(NO_2)_6$), and analysis was made on the cesium-enriched fraction. Perchloric acid is a useful reagent for concentrating the alkali metals with reasonable ease; for example, rubidium and cesium in ultrabasic rock types. The powdered specimen is treated with HF and $HClO_4$; silicon volatilizes as SiF_4. The perchlorates are taken to dryness and ignited for about twenty minutes at 550° C. For further details, see Marwin and Woolaver (1945). At this temperature, Mg, Al, and Fe are converted to oxides, whereas the alkali metals and the alkaline earths, Ca, Sr, and Ba, are converted to chlorides. Water extraction of the oxide-chloride mixture leaves the sparingly soluble oxides as a residue. The chloride solution is taken to dryness and arced. Some caution must be exercised when using perchloric acid because it reacts violently with organic substances.

Additional references: Tolmachev and Filippov (1936), Wager and Mitchell (1943), Nockolds and Mitchell (1948), Iwamura (1932 a), Iwamura (1938 a), Ahrens (1947), Ahrens and Liebenberg (1946), Patterson (1945), Erämetsä, Sahama, and Kanula (1941), Bertrand and Bertrand (1946), Sahama (1945 a and b), Oftedal (1940), Helz (1945).

CHAPTER 13

B; Be; Sr AND Ba

13–1. Boron. In the common igneous rock types, the concentration of boron (about 0.001%) is approximately equal to its limit of detection for most spectrochemical methods. Most silicate minerals contain about the same boron concentration. Because of its "borderline" concentration in many rock and mineral types, some analysts will report a trace of boron whereas others will record it as undetectable. In many sediments, however, there is a marked enrichment of boron, and here the enrichment is sufficient for its comparatively easy detection and estimation.

Boron has perhaps the simplest arc spectrum of any element. Most spectrochemists are aware of only two lines, the two sensitive doublet components B 2496.778 and B 2497.733. The latter is more sensitive and fortunately is relatively free from interference; even the SiO bands which cover much of the far ultraviolet (Section 10–2) are not strongly in evidence at this particular wavelength.

An omnipresent trace of boron in electrode carbon (Section 5–3) has caused many analysts to discard carbon (or graphite) electrodes in favor of copper. Goldschmidt and Peters (1932 c), who were the first to investigate the geochemistry of boron, used cathode layer excitation and copper electrodes. Attempts to purify carbon electrodes by heating them to 2700°C in the presence of N_2 and Cl_2 had proved unsuccessful. Although their method of analysis was semiquantitative, it was quite adequate for the purpose at hand. A more accurate method has been described by Landergren (1945), who employed antimony (added as 5% Sb_2O_5) as an internal standard. For the preparation of standards, boron was introduced as *tourmaline* to a boron-free feldspar. Because of the tendency of copper electrodes to melt, an intermittent arc was used. Because antimony is normally much more volatile than boron its choice as an internal standard for boron would at first sight appear to be a poor one. In the intermittent arc, however, selective volatilization is not so well developed, and the factor of volatilization rates is much less significant. Wasserstein (1943), who investigated the distribution of boron in manganese ores, also made use of copper electrodes.

For the analysis of boron in fertilizers, Melvin and O'Connor (1941) were able to use carbon electrodes free from a disturbing concentration of boron. This is reflected in the shape of their working curve. The linear relationship (log intensity ratio vs log concentration) is preserved over its whole length

despite admixture of two parts of carbon with each standard. A relatively high current (15 amp) arc was used and anode excitation was employed. Using beryllium as an internal standard, a good reproducibility was reported. Most analyses could apparently be made within ±5% of the mean.

The use of sugar as a source of boron-free carbon is described by Ermin and Dmitriev (1940).

Because the ionization potential of boron is high (8.28 volts), this element does not show marked cathode layer enrichment.

Additional references: Prokofev (1937), Sahama (1945, a and b), Smith and Hoagbin (1946), Gillis and Eeckhout (1947), Lundegardh (1946), Lundegardh (1947), McHargue and Calfee (1932).

13–2. Beryllium. Because of its very small size, Be^{++} (radius 0.34 A) is able to substitute for Si^{++++} (radius 0.39A) in silicates. Because the charge difference is two, only slight substitution is possible, however, and very small amounts of beryllium are found in the igneous rocks and silicate minerals. The concentration of beryllium is very near its limit of detection in these specimens — usually about 0.001–0.0001% when Be 2348 is employed. In many soils the concentration of beryllium is of this magnitude. Beryllium tends to enrich in minerals of relatively late formation in pegmatites. In these the less sensitive but more conveniently placed doublets Be 3131.072 and 3130.416 or Be 3321.342 and $\begin{cases} 3321.086 \\ 3321.013 \end{cases}$ may be used.

Many analysts have recorded observations on the behavior of beryllium line intensities in different matrices. Goldschmidt and Peters (1932a) found that the intensity of Be 2348 for a given beryllium concentration was the same in quartz, alumina, and in synthetic and natural *olivine*. Fesefeldt (1929) investigated the analysis of beryllium and used an alumina base. The presence of added Na_2CO_3 influenced line intensity, that of CaO did not. Kemula and Rygielski (1933) observed that in the presence of an element of low ionization potential, the intensities of beryllium lines weakened considerably. The degree of weakening could be correlated with the ionization potential of the added element. Thus, of the elements examined, the order of weakening was as follows: K > Na > Ba > Ca > Mg > Al > Si. Intensity was highest in a silica matrix and lowest in the presence of a potassium salt. This is not surprising, because the excitation potentials of all beryllium lines are relatively high. On the other hand, Marks and Jones (1948) investigated the influence of compositional variation on the intensity of Be 3321 and found its intensity to be independent of the composition of the matrix. They employed the "total energy"

method of Marks and co-workers (Chapter 11) for the determination of beryllium in ores. An automatic current regulator was used to maintain a constant current (Section 4–2).

For the determination of beryllium in sedimentary rocks, Pieruccini (1943) attempted the use of iron as an internal standard. The line pairs were Be II 3131 or 3130 and Fe II 2984; Be I 2348 and Fe I 2320. Cathode layer excitation was employed, and the observation was made that whereas most lines of other elements emitted their greatest intensities immediately adjacent to the cathode, those of beryllium emitted theirs about 3–4 mm above it. Plate 4 shows a similar observation made in the Cabot Spectrographic Laboratory on Be 3131:3130, two ion lines. The longitudinal intensity distribution of this doublet is quite different from that of other lines, and the maximum intensity is a considerable distance from the cathode. In Plate 4 this effect can best be seen by examining the ghost lines. Cathode layer enrichment is not very marked because the ionization potential of beryllium is very high (9.28 volts).

In minerals and rocks, beryllium is usually much less volatile than the other alkaline earths, and is a typically involatile element.

Additional references: Rusanov (1936), Oftedal (1940), Stoll (1945), Sahama (1945 a and b), Perry and Cooke (1946), and Watson (1947).

13–3. Strontium and barium. Although strontium and barium are not rare elements, their concentrations in most minerals and rocks are nevertheless just low enough to make chemical analysis difficult and tedious. Most routine chemical analyses do not include these two elements. They may, however, be detected and estimated spectrochemically with reasonable ease. Strontium and barium have high spectral sensitivity, and the limit of detection is about 0.001–0.0001%.

Strontium and barium form the largest of all multivalent cations and are capable of replacing Ca^{++}, Na^{+} and K^{+}, in their minerals. Because of a similarity in the radii of Sr^{++} and Ca^{++} (1.27 A and 1.06 A respectively), strontium is readily accepted in calcium minerals, whereas the larger Ba^{++} (radius 1.43 A) is admitted less freely in calcium minerals and favors replacement of K^{+} (1.39 A) in potassium minerals. Sr^{++} is also admitted into potassium minerals, but usually to a lesser extent than Ba^{++}. Strontium and barium are thus geochemically associated in many of the common silicate minerals. Occasionally, however, only strontium may be found, as in certain rubidium-rich potassium minerals such as *lithium mica*. Here strontium is a product of β-decay of rubidium, and is not associated with barium; the barium concentration may be less than 0.0001%.

The spectrochemistry of strontium is similar to that of barium and of calcium. Each element is of medium-late volatility in minerals and rocks,

and each emits sensitive lines from both atom and ion. In a relatively cool arc, the respective low-temperature arc lines Sr 4607, Ba 5535, and Ca 4246 are the most sensitive, whereas in a high-temperature arc, for example one between impure electrodes, the ion lines Sr 4077 (CN emission must be depressed), Ba 4554, and Ca 3933 are the most sensitive. In general, a spectrochemical procedure that is satisfactory for strontium will also be satisfactory for barium and calcium.

Of the three most sensitive lines of strontium which are available, the analyst may occasionally be forced to use Sr 4077. Thus Ahrens (1949), while determining strontium in various minerals (notably *lithium mica*), found that Sr 4607 was excessively masked by Li 4603 when quartz optics were employed. Sr 4215 could not be used because of coincidence with Rb 4215 and the use of Sr 4077 was attempted. If a specimen of *mica* is arced to completion, however, CN emission is low at first because of the presence of the alkali metals and then increases sharply during the late arcing period when Sr 4077 emits its peak intensity. This is shown in Fig. 13–1. CN interference is excessive and it is impossible to use Sr 4077. If the constituents of the *mica* are converted to fluorides, however, CN emission can be cleared during the whole period of arcing (Section 10–2) and Sr 4077 may be used.

For most purposes, Sr 4607 can be used. This line was employed by Strock (1942) for the determination of strontium in *mica*. In this paper considerable attention is given to the preparation of standards and corrections for impurity.

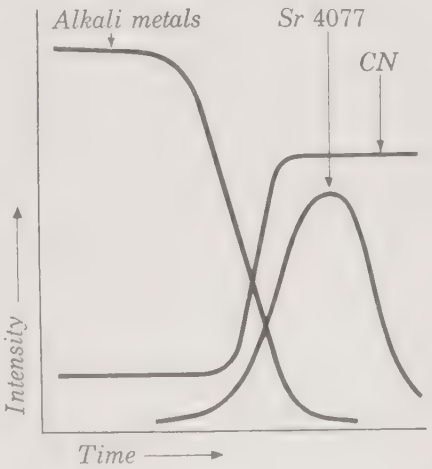

Fig. 13–1. After the volatilization of the alkali metals, Sr 4077 emits its peak intensity, but this may be swamped by CN emission, which also develops after the volatilization of the alkali metals.

Strock and Heggen (1947) attempted the analysis of Sr, Ba, Mg, and Ca in residue from brine solution. Anode excitation was employed, and the use of beryllium as an internal standard was tried. The reproducibility was not satisfactory; this could be attributed to a large difference in the volatilization rates of internal standard and analysis elements. Beryllium was far more involatile than the other elements and emitted its peak intensity only after the bulk of the other elements had volatilized. Chromium was found to volatilize in much the same way as the analysis elements, and through its use a much greater reproducibility could be attained.

Bray (1942) has attempted the use of palladium as an internal standard

for the determination of strontium and barium (Chapter 11). The method was applied to the study of Sr/Ba ratios in various minerals and rocks.

A method which involves a preliminary chemical concentration is described by Hybbinette (1943) for the analysis of relatively small strontium concentrations (0.01% and less). After dissolution of the specimen, the usual oxalate precipitation is made in the presence of an excess of added calcium. The copious precipitate of calcium oxalate serves to collect strontium. After ignition a spectrochemical analysis is made, using calcium as the internal standard. As calcium is an ideal internal standard for strontium, spectrochemical reproducibility should be good, but at relatively low concentrations of strontium, incompleteness of its separation in the carrier precipitate may be a cause of serious error. A statement by Hybbinette that the chemical concentration was necessary because of the low spectral sensitivity of strontium cannot be accepted, because strontium is very sensitive.

Von Engelhardt (1936) used cathode layer excitation for the determination of barium in minerals and rocks. The synthetic standards (barium glass + quartz as base) and unknowns were buffered with NaCl (one part) which contained lanthana as the internal standard. The ion line pair Ba 4554 and La 4558 served as the analysis pair. The sensitivity of the intensity ratio of the analysis pair to compositional changes was examined. In the presence of relatively large amounts of Al, Fe, and Ca silicates, NaCl buffered effectively and no appreciable effect was noticed. However, when calcium was present as a carbonate, the intensity ratio was disturbed. Fig. 13–2 shows the effects of varying amounts of $CaCO_3$ added to quartz on the intensity ratio Ba 4554/La 4558. Each specimen contains NaCl + La_2O_3, as above. As a consequence, one series of standards might be used for silicates and another for carbonates.

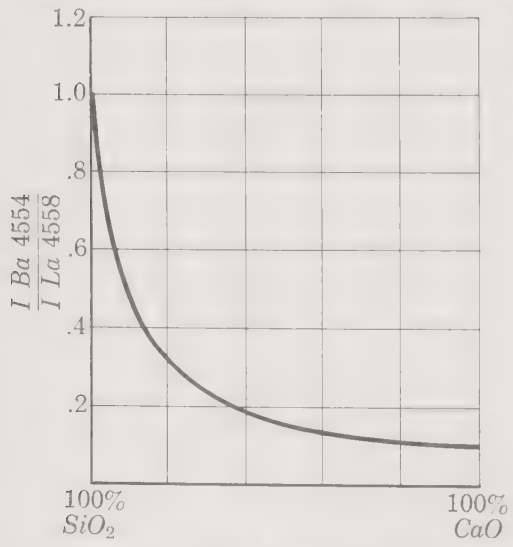

Fig. 13–2. This diagram shows that the presence of CaO (or $CaCO_3$) depresses the intensity ratio Ba 4554/La 4558 very markedly. In other matrices (silicates of Al, Ca, and Fe) no effect was observed. The anion apparently plays an important role.

Additional references: Hukuda (1927), Wager and Mitchell (1943), Nockolds and Mitchell (1948), Patterson (1945), Noll (1934), Van Tongeren (1938), Calkins and White (1946), Sahama (1945 a and b), Lundegardh (1946), Fast and Nielson (1947).

CHAPTER 14

F AND Cl

14–1. Fluorine. The d.c. arc does not furnish sufficient energy to excite fluorine (excitation potential of lowest energy line = 14.3 volts), but an analysis of this element may nevertheless be made in this source by excitation of the molecular emitters CaF or SrF. Fluorine is not normally regarded as a rare constituent in many minerals, rocks, and soils, but due to the tedium of its analysis by chemical procedures, fluorine is rarely reported in most standard chemical analyses. The use of a rapid spectrochemical method is therefore of much value. In many so-called basic rock types, the fluorine concentration is about 0.01–0.02%, which is near the limit of spectral sensitivity. Many of the more acid rock types contain roughly 10× this amount, and this can easily be detected and estimated. Favorite host minerals of fluorine are those which contain the radical $(OH)^-$, which is replaceable by F^-; $(OH)^-$ and F^- have similar radii.

The use of the CaF band with head at 5291 A was first suggested by Ryde and Yates (1926) and was thereafter applied to the analysis of fluorine in minerals by Papish, Hoag, and Snee (1930).

The diatomic molecular emitter CaF is easily excited, and the excitation potential of CaF 5291 is only a few volts. However, if the source is a very vigorous one, the molecule dissociates and there is thus no CaF excitation in sparks, nor is the hot central core of the arc a zone favorable for its emission. CaF emission develops most readily in the outer fringe of the arc, and in general a cool flame-like arc is most conducive to its emission.

The band component at 5291 A is the head of a sequence in which many other components are about equal in intensity to 5291 A. Some of these components are 5292.9, 5296.8, 5298.6, and there are many others. Any of these may be used for analysis. Plate 4 shows the sequence with head at 5291 A taken with quartz optics.

The emission of CaF 5291 develops irrespective of whether fluorine is originally combined with calcium in the specimen or not. If the specimen contains no calcium, it must be added either as the oxide or a salt. Some analysts, for example Hughes (1946), have used electrodes steeped in saturated $CaCl_2$. To obtain optimum sensitivity, calcium should be present in the arc column in excess. As yet, however, there is no information on how much calcium in the arc column is necessary to ensure a maximum intensity of CaF 5291 at a given concentration of fluorine. Fluorine is very volatile, whereas calcium is much less so, and any factor

which accentuates this difference in volatility may bring about a lowering of sensitivity.

Consider a specimen of *phosphate rock* which contains about 0.5% fluorine, one portion diluted with one part powdered carbon, and another with one part of KCl. Each is arced to completion using anode excitation (7 amp) in a relatively large anode cavity which will accommodate about 100 mg of sample. At intervals of 15 seconds the plateholder is racked down. Fig. 14–1 (A) and (B) show volatilization curves for CaF 5291 and also lines of Ca, K, Fe, Si, and Ti. The general depressant influence of the presence of potassium is quite evident (Fig. 14–1 (B)) and all elements begin to emit strongly only after the bulk of potassium has distilled. As a result there is a paucity of calcium atoms in the early period of arcing, during which volatile fluorine is vaporized and all that can be observed of CaF 5291 is a doubtful haze. In the presence of carbon (Fig. 14–1 (A)), however, all elements are made readily volatile during the early period of arcing. Much calcium is present and CaF 5291 is strongly in evidence. In a 1:1 mixture of carbon and phosphate rock, carbon tends to burn off before complete volatilization of the sample, and after the volatilization of carbon, regular selective volatilization of the elements is again evident, as may be seen in Fig. 14–1 (A).

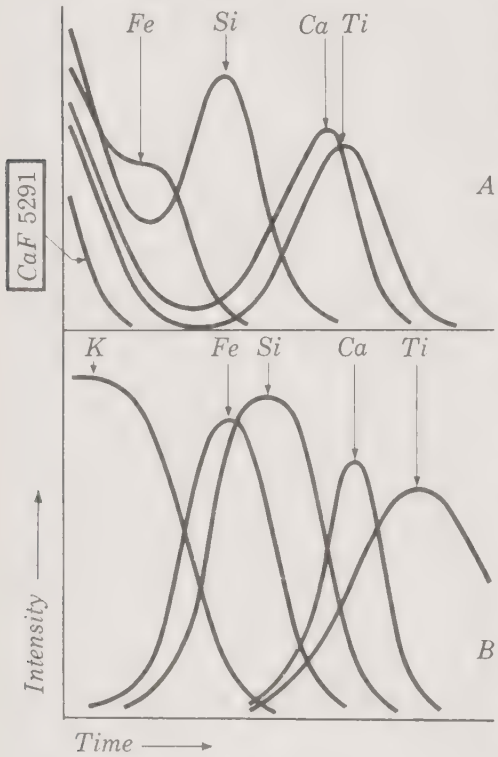

Fig. 14–1. Selective volatilization curves for several elements in phosphate rock, (*A*) in the presence of powdered carbon and (*B*) in the presence of KCl. Note the depressant effect of KCl, as a result of which calcium is so depressed during the early period of arcing that no CaF emission has been recorded.

The observations on the behavior of the intensity of CaF 5291 in *phosphate rock* apply generally. Selective volatilization plays a major role here in affecting the sensitivity of the test, and steps must be taken to ensure a copious release of calcium atoms during the early period of arcing. To meet this requirement the addition of two parts of a mixture of 70% powdered carbon + 30% $CaCO_3$ to each specimen is recommended.

The use of a low amperage seems unsatisfactory because selective

volatilization is accentuated. If cathode layer excitation is used, sensitivity is poor. The highest sensitivity is attainable when anode excitation and a deep anode are employed. Harrison (1949) has had success with a mixture of $NH_4Cl + CaCO_3$. He found that whereas the use of a $C + CaCO_3$ mixture added to a lead halide mineral failed to show CaF 5291, the use of added $NH_4Cl + CaCO_3$ proved successful.

Little information on the quantitative analysis of fluorine is available in the literature. Ahrens (1942) determined fluorine in phosphate rock of various grades in an ore dressing laboratory and used chemically analyzed specimens as standards. Triplicate exposures of 15 seconds were made and, using a logarithmic sector, a standard deviation of approximately $\pm 15\%$ was obtained. For most rocks greater exposures (1–2 minutes) are usually used because fluorine is not volatilized quite so quickly from them as from phosphate rock.

One example of the application of the spectrochemical method of fluorine analysis is given by Walker, Ahrens, and Gorfinkle (unpublished data). Fluorine was determined in several specimens of diabase from the Palisades, New York. In most about 0.015% was found. These specimens contain a mean of about 0.15% P_2O_5 and the ratio $\%P_2O_5/\%F$ averages therefore at about 10. In two specimens, a much higher fluorine content was found, namely, 0.05 and 0.13%. These two specimens, however, were the only ones which showed the presence of *amphibole;* respective modes, 1.7 and 4.1. This is corroborative evidence of a geochemical rule which states that in most basic rocks the ratio $\%P_2O_5/\%F$ is roughly constant and $= \sim 10$, unless there is development of *amphibole*, in which case the fluorine content is likely to vary with the amount of *amphibole.*

No attempt has yet been made to use internal standardization for the accurate analysis of fluorine. Such a procedure seems quite feasible, however, provided the internal standard element is very volatile and the internal standard line has a low excitation potential.

Molecular spectra show self-absorption at high concentrations, and in quantitative determinations such a possibility should be considered for CaF 5291.

The components of the 5291 band are not very sharp or narrow and the use of a very large dispersion produces rather diffuse band lines, thereby lowering sensitivity. Optimum sensitivity is probably attainable when a prism or small grating spectrograph is used.

Ahrens (1943 a) has reported the use of bands emitted by SrF as an alternative to CaF 5291 for detecting and estimating fluorine. Of the bands emitted by SrF, the one with a head at 5772.0 A is the most sensitive. This band is shown in Plate 4. It has a sharp head and is equally sensitive to CaF 5291. SrF 5772 can be used in exactly the same way as CaF 5291.

In general, however, the use of CaF 5291* is preferable for the analysis of fluorine in minerals, rocks, and soils, because a high proportion contain appreciable amounts of calcium. When a strontium salt is added, both CaF 5291 and SrF 5772 are emitted; thus the available number of fluorine atoms is distributed between the two emitters and sensitivity is lowered.

Fairly intense bands are also emitted by BaF, but they are not as clearly defined or as sensitive as CaF 5291 and SrF 5772 (Ahrens, 1943).

Additional references. Churchill (1931), Petrey (1934), Peterson, Kauffman, and Jaffe (1947).

14–2. Chlorine. According to recent spectroscopic (visual) evidence, bands emitted by CaCl may be utilized for the detection of chlorine in minerals (Jaffe, 1949). The most sensitive bands have heads at 6211.6 and 5934.0 A. Both are degraded to the violet, and of the two bands CaCl 5934 seems better suited for the detection of low concentrations of chlorine.

The excitation potential of these bands is low and the molecule CaCl dissociates readily in high energy sources. Consequently the conditions most favorable for the emission of CaCl 6211 and 5934 are found in the flaming fringe of the arc. CaO or a salt of calcium must be added to the specimen if it is not calcium-rich. The general discussion on the importance of selective volatilization for the CaF 5291 test for fluorine applies here also, because chlorine is much more volatile than calcium.

Jaffe has been able to detect chlorine in several minerals. He found that by using CaCl 5934 and CaF 5291 it was possible to differentiate quickly between the chlor- and fluor- varieties of *apatite*.

Bromine and iodine also form molecular emitters with some of the alkaline earths. These molecules dissociate rather readily in the arc and only feeble emission, if any, is observable. A flame source is probably better suited to their emission.

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* Recent work at the Cabot Spectrographic Laboratory has shown CaF 6064 (degraded to the violet) to be much more sensitive than CaF 5291. CaF 6064, however, tends to be masked by intense CaO bands (orange systems).

CHAPTER 15

Ga; In; Tl

Each of these group III-b elements was discovered spectroscopically and each has interesting geochemical properties. Much of our present-day knowledge of their distribution and abundance in the earth's crust is based on the results of spectrochemical analyses. Dual geochemical behavior is a characteristic of the group, and each element distributes itself in many of the silicate minerals as well as in sulfides. In this respect they are similar to Pb, Zn, Ni, Ge, and a few other elements. A high spectral sensitivity is characteristic of the group.

15–1. Gallium. Gallium is one of the most ubiquitous of the rarer elements, and its concentration remains remarkably uniform in a very wide variety of minerals and rocks. The cause of this uniform distribution of gallium is its association with aluminum. Both elements have similar chemical properties, and since the radius of Ga^{+++} (0.62 A) is very similar to that of Al^{+++} (0.57 A), Ga^{+++} enters aluminum minerals with facility. Aluminum is, of course, a major component in a very wide variety of minerals. In the aluminum minerals, rocks, and soils, the concentration of gallium usually lies within 0.001 and 0.01%. Consequently gallium can be detected and estimated in many specimen types because its limit of detection is at least 0.001%, and as little as 0.0001% can often be detected.

Fig. 15–1 illustrates to some extent what is meant by a relatively uniform distribution of gallium. It is a plot of log % Ga_2O_3 found in each of several

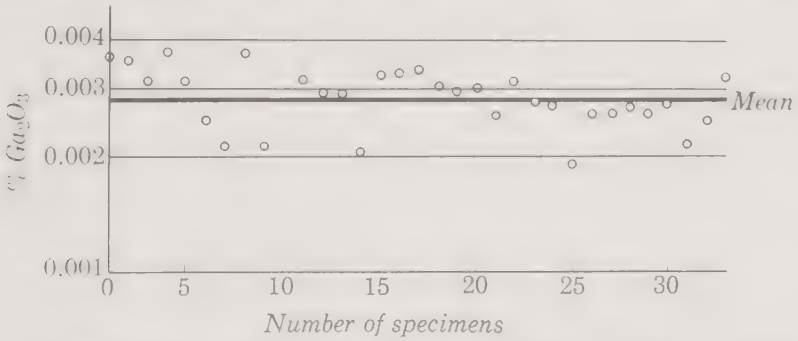


Fig. 15–1. This figure illustrates the comparatively uniform distribution of gallium in 33 basic rock types (mainly diabase). Most points fall within ±25% of the mean. Nearly all other elements fluctuate very much more in these specimens, often by factors of 10 or more. Scandium is one exception (Section 17–1).

basic rocks (mostly diabase types) vs the number of specimens. Whereas the concentrations of almost all other minor constituent elements fluctuate considerably, frequently by factors of 10 or more in these specimens, the Ga_2O_3 concentration is usually within about $\pm 25\%$ of the mean.

Ga 4172 is the most sensitive line of gallium, but is not in common use because of possible interference from CN 4216. However, gallium is relatively volatile and CN emission can be cleared sufficiently to make the use of Ga 4172 possible (Section 10–2). The added alkali metal salt not only clears CN emission but creates an arc environment which usually enhances the intensity of gallium lines. It has become quite common practice to add an alkali metal salt when attempting to detect and estimate gallium unless, of course, the sample contains a high concentration of alkali metal. The next most sensitive gallium line, Ga 4033, is almost useless because of ever-present interference from sensitive Mn 4033. Ga 2943.6 has been used by many analysts, who find its sensitivity sufficient for the analysis of gallium in most common minerals, rocks, and soils.

Many semiquantitative procedures for the analysis of gallium have been described. See, for example, Goldschmidt and Peters (1931 a), van Tongeren (1938), and Mitchell (1948). However, only a few publications report attempts to determine gallium accurately in silicates through the use of internal standardization. One such method is described in Chapter 11, where indium is the internal standard element.

Strock (1945) determined gallium in zinc sulfide ores, using beryllium as an internal standard; each specimen was buffered with NaCl. Two cathodes were used, one of $\frac{1}{16}''$ and the other of $\frac{7}{16}''$ diameter. Crater depth was about the same for each (4–5 mm). A separate working curve was constructed for each electrode size, and these curves, although parallel, were found to be displaced considerably. In the large anode the intensity ratio of the analysis pair Ga 2943 and Be 3130 was found to be about $4\times$ greater than in the smaller electrode. As a result, Strock emphasizes the need to keep electrode dimensions constant. Oftedal (1941) also employed internal standardization for the analysis of gallium in zinc sulfide. The line pair Ga 2943 and Zn 3282 was used and cathode layer excitation was employed. Oftedal remarks that Ga 2943 showed a very strong development of cathode layer enrichment. Others have noted that gallium lines exhibit a marked cathode layer development.

Additional references: Borovik and Sosedko (1937), Cambi and Maletesta (1936), Kuzmina (1938), Bertrand (1941), Ahrens (1945 a and c), Borovik (1941), Rusanov and Alekseeva (1940), Stoll (1945), Wager and Mitchell (1943), Evrard (1945), Stoiber (1940), Szelényi and Vogl (1941), Nockolds and Mitchell (1948), Lundegardh (1946), Sahama (1945 a and b), Abramov and Rusanov (1938), Kimura and Koyama (1936).

15–2. Indium. Although indium has a very high spectral sensitivity, it is rarely possible to detect it spectrochemically in the common silicate minerals, rocks, and soils. Indium is more than 100 times rarer than gallium. Of the commoner silicate minerals, *mica* and *amphibole* occasionally show detectable concentrations of indium. Here In^{+++}(radius 0.92 A) probably occurs octahedrally. Indium can frequently be detected in sulfide minerals, notably *sphalerite*, and also in *cassiterite* (SnO_2).

Low amperage anode excitation was used by Ahrens and Liebenberg (1950) for the analysis of indium in *mica*. A limit of detection of 0.00003% is reported. This concentration is somewhat lower than has been reported by other analysts, but it should be possible to detect a concentration as low as 0.0001% indium. In lithium mica, appreciable traces of manganese cause detectable emission of Mn 3256, which interferes with In 3256. Correction can, however, be made for such interference as described in Section 9–8, and is facilitated by a large difference in the volatilization rates of indium and manganese. Indium is much more volatile than manganese (Section 6–4).

In 4511, which is a little more sensitive than In 3256, was used by Ahrens (1948) for the analysis of indium in *cassiterite*.* According to the M. I. T. tables there is a relatively intense (intensity of "200" given) tin line at 4511.30 A. This line should, therefore interfere with In 4511.323. In the spectrum of the ancient *cassiterite*, which contains tin as a major constituent, all that could be seen at λ 4511 A was a doubtful haze, due possibly to In 4511. There is therefore no strong tin line at λ 4511 A, and there may be no such tin line at all. In the M. I. T. tables reference is made to Arnolds (1914) as the source for this measurement.

Although indium cannot be detected and estimated in the common silicate minerals, rocks, and soils using standard spectrochemical procedures, use may be made of the furnace techniques as described in Section 5–5. The use of combined chemical enrichment and spectrochemical analysis offers another procedure for determining very low concentrations of indium. Prokopenko (1941) treated 10–100 gm of rock specimen with $HF+H_2SO_4$. After taking to fumes of SO_3, dilution, and filtration, NH_4OH was added to neutralize the filtrate, which was then saturated with H_2S. The sulfide

* The presence of indium in this mineral has quite often been reported. These reports have caused speculation by nuclear physicists on the possible radiogenic origin of such indium. The existence of Sn^{115} and In^{115} violates the nuclear stability rule of neighboring isobars; the presence of indium in some cassiterite appears to provide corroborative evidence of predicted electron capture decay of $Sn^{115} \rightarrow In^{115}$. However, a very ancient (2000×10^6 years) cassiterite specimen was analyzed using In 4511 and only a doubtful trace ($\sim 0.0001\%$) of In_2O_3 was found. This low concentration of indium indicates that, contrary to the expectations of some, Sn^{115} has undergone no significant decay during geological time.

precipitate was analyzed spectrochemically. The method has been applied to the analysis of indium in many rock types, soils, and several minerals.

Marks and Jones (1948) have described the use of a "total energy" method for the analysis of indium in sulfide ores (Chapter 11). Oftedal (1941) and Strock (1945) also describe methods for the analysis of indium in *sphalerite* and other sulfides. Both comment on the enhancement of the intensity of indium lines in the presence of a sodium salt. This behavior of indium is similar to that of gallium, and Strock contrasts the behavior of Ga and In with that of Cd, Sb, and Hg. Under the same conditions of arcing, the presence of alkali metal was found to depress the intensities of the lines of cadmium, antimony, and mercury.

Like gallium, indium is relatively volatile, and usually to a somewhat greater extent.

Additional references: Papish and Holt (1930), Borovik, Prokopenko, and Pokrovskaya (1939), Erämetsä (1938), Borovik and Gotman (1939), Rusanov and Alekseeva (1940), Stoiber (1940), Szelényi and Vogl (1941), Brewer and Baker (1936), Cambi and Maletesta (1936), De Azcona (1942), Kimura and Koyama (1936), Itsikson and Rusanov (1946).

15–3. Thallium. Soon after the discovery of thallium, chemists recognized the unusual chemical properties which led Dumas to dub it the *ornithorhynchus* (the duckbilled platypus) of the elements. Several of its properties are similar to those of Ag, Pb, and Cu, whereas others closely resemble those of the alkali metals of high atomic weight. As a result, thallium exhibits a very marked dual geochemical behavior. It is frequently present as a trace in many sulfide minerals with Ag, Pb, and Cu; on the other hand, because Tl^+ is a virile cation of radius 1.49 A, it is found in detectable amounts (0.0001 – 0.02%) in all potassium minerals. In these Tl^+ replaces K^+. Because the radius of Tl^+ is greater than that of potassium, thallium enriches considerably in late hydrothermal minerals in much the same way as rubidium (Section 12–2). In fact, since the radii of Rb^+ and Tl^+ are identical, their association in these minerals is extremely close.

Although thallium is easily detected in all potassium minerals, its concentration in most common rocks, even those rich in potash, is usually a little below the detection limit. Likewise, thallium concentration in many soils is below detection, although in some potash-rich varieties it can be detected. In nearly all rocks, minerals, and soils, use may be made of the furnace techniques for the analysis of thallium (Section 5–5).

The most sensitive lines of thallium are Tl 5350 and Tl 3775. Tl 3775 is of a convenient wavelength, but it has received very little attention because of possible interference from the CN band with head at 3883 A.

Van Tongeren (1938) used it, but reported a poor detection limit of 0.01%. Ahrens (1945 b) has used Tl 3775 extensively for the analysis of thallium in potassium minerals. Provided CN emission was quenched and alkali metal vapor was present in the arc, less than 0.0001% thallium could be determined. Low amperage anode excitation was employed. As thallium was sought in potassium-rich minerals, it was not necessary to add potassium compound to help clear CN emission. A trace of interference from one of the band components madeitself evident at very low concentrations of thallium, however, and this is shown in the working curve of Fig. 15–2. Background correction has been made but there is nevertheless a very marked toe. A careful examination of some plates has shown that the interference is probably caused by a component of the CN band with head at 3883 A, which is almost exactly superimposed on Tl 3775.

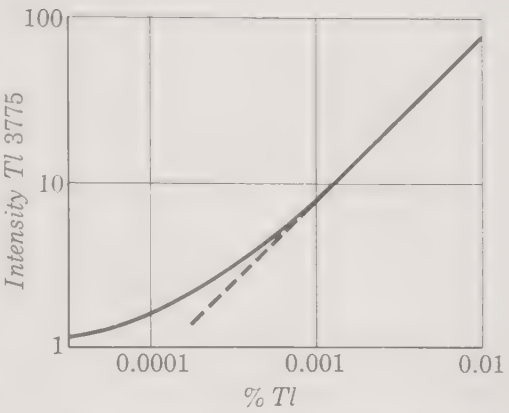


Fig. 15–2. A working curve for the determination of thallium, using Tl 3775. Despite accurate correction for background and for possible contamination, a toe is evident in this curve. The cause has been found to be the presence of a rotational component of the CN band with head at λ 3883 A.

Some analytical data (Ahrens, 1945 b) are given in Table 15–1 to provide an indication of the reproducibility of the method at low thallium concentrations. No internal standardization was employed. A cutoff arcing procedure had to be used because if the specimen had been arced to completion, CN emission would have swamped Tl 3775.

Table 15-1

No.	% Tl in feldspar specimen	% deviation from mean
1	0.00047	+12
2	0.00040	- 5
3	0.00036	-14
4	0.00036	-14
5	0.00039	- 7
6	0.00044	+ 5
7	0.00052	+25
8	0.00039	- 7
	Approx. std. dev.	±14%

No attempt was made to improve this reproducibility, because it was adequate for the purpose at hand.

In basic rock types Ni 3775.572 is easily detectable and will cause interference, but in these rocks the thallium concentration is so low that Tl 3775 is not likely to be present; even Tl 5350 cannot be detected. In some sulfide minerals where thallium is present in detectable amounts, interference of Ni 3775 with Tl 3775 is likely.

Tl 5350 has been used by Marks and Hall (1949) for the determination of thallium in ores. A "total energy" method was employed (Chapter 11). In place of the usual lime buffer used by Hall and co-workers, $BaCO_3$ was used, because its buffer action was equally effective and a smoother arc burn was produced. In the presence of Na_2CO_3 and K_2CO_3, Tl 5350 showed a marked intensity increase, and these authors suggest interaction of energy levels (collisions of the second kind) as the cause. The lower level of Tl 5350 is a metastable one, 0.96 volt above the ground state. However, cognizance should also be taken of the fact that the sensitive lines of all three group III-b elements, including Tl 3775, often emit their maximum intensities in the presence of alkali metal vapor.

In common with Ga and In, Tl is volatile. Its volatility is greater than that of either Ga or In.

Additional references: Schröder (1932), Ottemann (1940), Shaw, Joensuu and Ahrens (1950), Kimura and Koyama (1936), Sempels (1948).

CHAPTER 16

THE RARE EARTH ELEMENTS (Y AND ELEMENTS 57–71)

The rare earth elements form a geochemically coherent group whose commoner members can often be detected and determined spectrochemically in a wide variety of minerals, rocks, and soils. As a time-saving procedure in analysis, these most common members are sought first, and if they are absent, it is safe to assume that the others are absent also. Fig. 16–1, which gives a typical relative abundance plot of the rare earth elements in a specimen of granite, shows Y, Ce, La, and Nd as the commonest rare earths. It may readily be seen in Fig. 16–1 that the rare earths of even atomic number are more abundant than those of odd atomic number (Harkins Rule). Although the abundance relationship between various rare earth elements varies somewhat in different minerals, rocks, and soils, the group is usually sufficiently coherent to preserve the general abundance-relationship pattern depicted in Fig. 16–1, which may serve as a guide to the analyst. Reference may be made to Sahama and Vähätalo (1939) for plots similar to Fig. 16–1 of various rock specimens.

In rocks, several calcium minerals are common hosts for the rare earth elements; *titanite* (*sphene*), *apatite*, and *fluorite* all show a characteristic enrichment of the rare earth elements. These elements are able to enter

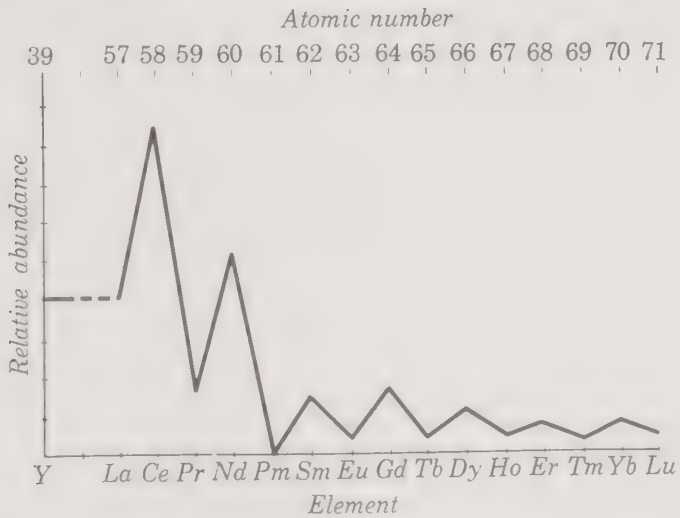


Fig. 16–1. Approximate abundance relationship between Y and the members of the rare earth group in the earth's crust. The commonest rare earth elements are Y, Ce, La, and Nd.

the structures of calcium minerals with facility because their ionic radii (1.00–1.22 A) are very similar to that of Ca^{++} (1.08 A). Nockolds and Mitchell (1948) give many analyses of Y and La in minerals separated from common igneous rocks. See also Bray (1942) and Shimer (1943).

As a group, the rare earth elements exhibit a reasonably high spectrochemical sensitivity and a detection limit of about 0.001% applies to many of them. Ce (see below), Sm, and Gd are exceptions and are less sensitive. Y and La are the most commonly reported rare earth minerals in rocks, minerals, and soils; Nd is sometimes reported, and others very rarely unless preliminary chemical concentration has been used.

Van Tongeren (1938) has made many analyses of cerium in rocks, using Ce 4222, one of the most sensitive cerium lines. He claims a detection limit of 0.002% for this line. This observation does not accord with those of several other workers. Thus Mitchell (1948), who also used Ce 4222 and cathode layer excitation, reports a detection limit of only 0.05%; this concentration is above that of cerium normally present in rocks and soils. Observations in the Cabot Spectrographic Laboratory, M. I. T., have also shown relatively poor sensitivity for cerium using this line, and it has been impossible to detect cerium in rocks thus far examined. Ce 4186 is probably a little more sensitive, but is masked by CN emission. In the Cabot Spectrographic Laboratory, lanthanum has been determined in many rocks through the use of La 4333. La 3949 may be a little more sensitive than La 4333, but is not used because background often interferes considerably.

Y 3710.29 is the most sensitive yttrium line, but is liable to some interference from CN emission as it coincides with a rotational component of the band with head at 3883 A. Provided that the method of arcing has not caused excessive CN emission, Y 3710 may be used for the determination of yttrium in granitelike rocks. A correction will frequently be necessary, however, and in the Cabot Spectrographic Laboratory, Mrs. L. G. Gorfinkle has employed this procedure. The intensity ratio of CN 3710.3 to a neighboring CN component (CN 3710.55) was determined in the absence of yttrium as 0.67. In the analysis of an unknown, correction is applied by subtracting 0.67 $\times$ intensity of CN 3710.55 from $\left\{ \begin{matrix} \text{Y} \\ \text{CN} \end{matrix} \right.$ 3710.3. The validity of this correction is shown by the working curve plots in Fig. 16–2. Here two curves are shown; in one, no attempt at correction has been made and at relatively low concentrations this curve becomes asymptotic with the abscissa. The other shows the curve obtained after a correction has been made for interference from CN 3710. The shape of this working curve appears normal. Provided a correction is made this way, Y 3710 may be employed for concentrations down to about 0.001 –0.003% Y_2O_3,

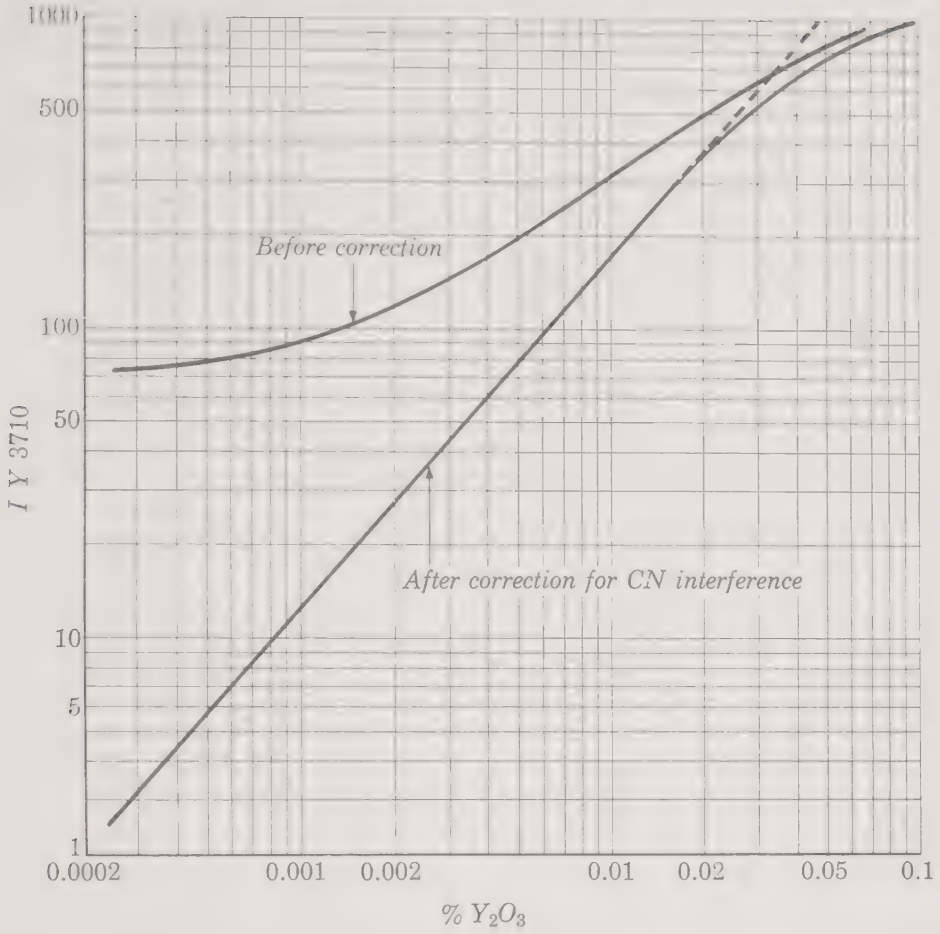


Fig. 16–2. Working curve for Y 3710 showing its form after correction for CN band interference has been made.

using the operating procedure outlined in Chapter 11 (method employing palladium as internal standard). Depression of CN emission by the method of Wiggins (1949) or by any of the other methods listed in Section 10–2 would increase the sensitivity of Y 3710 very considerably.

Y 4374.935 is very sensitive and has been used by Sahama and Vähätalo (1939). There is, however, danger of interference from Mn 4374.947. Such interference is not usually definitely evident in granitic rocks, but in basic rock types, a relatively strong line which appears at λ 4374 is evidently due to manganese. Y 3242.28 is a fairly sensitive ultraviolet line and enables the analyst to detect and determine yttrium in granitelike rocks. A large dispersion is necessary, otherwise there will be interference from Ti 3241.986.

Nd 4303 is probably the most sensitive line of neodymium. Its use has been recommended by van Tongeren (1938) for the analysis of neodymium

in minerals and rocks. In the Cabot Spectrographic Laboratory, M. I. T., this line has been used quite extensively. It was found, however, that in basic rocks Nd 4303 appeared surprisingly intense compared with its intensity in granitelike rocks. This did not accord with the fact that granitelike rocks contain appreciably higher concentrations of rare earths than the basic varieties. No possible interfering line could be found in the M. I. T. tables, but an inspection of the original cards showed the listing of an iron line (Fe 4303.585) with an intensity of "25"; this line had apparently been accidentally omitted from the tables. The arc spectrum between iron electrodes shows a line at λ 4303. Nd 4303 should therefore not be used in iron-rich specimens.

Even in rocks comparatively low in iron, caution must be exercised. Observations made in the Cabot Spectrographic Laboratory by Mrs. L. G. Gorfinkle show that the amount of interference in granitelike rocks is usually about 40–70%, when using the general method described in Chapter 11 (Pd as internal standard). This is very considerable, but an indication that the use of a correction method* works reasonably well is shown by the following analyses of Nd, La, and Y in granite. It is known that Nd is very closely associated with La and that in granitelike rocks the ratio La_2O_3/Nd_2O_3 averages about 1.0; for individual specimens this ratio usually lies within 0.5 and 2.0. Seven analyses of Nd_2O_3, La_2O_3, and also Y_2O_3, are given in Table 16–1. The general abundance of Nd in these rocks appears normal, as does the ratio La/Nd. It is known also that Y has an abundance similar to that of La and Nd. The data in Table 16–1 agree with this statement and provide further indirect evidence that the method of correcting for CN interference with Y 3710, as just discussed, is reasonably accurate in granitelike rocks.

Table 16-1

Locality		$\%Nd_2O_3$	$\%La_2O_3$	$\%Y_2O_3$	$\frac{\%La_2O_3}{\%Nd_2O_3}$	$\frac{\%La_2O_3}{\%Y_2O_3}$
Contact Lake	Can.	0.0080	0.0078	0.0083	1.0	0.95
Conjuror Bay	Can.	0.0060	0.012	0.011	2.0	1.1
White Eagle Falls	Can.	0.0053	0.0029	0.0054	0.55	0.55
Great Bear Lake	Can.	0.0080	0.0056	0.0050	0.70	1.1
Great Bear Lake	Can.	0.0050	0.0051	0.0041	1.0	1.2
Handley Page Lake	Can.	0.0030	0.0039	0.0080	1.3	0.5
Westerly, R. I.	USA	0.0093	0.015	0.0030	1.6	5.0

* See Section 9–8 for discussion of general method of correction. In above example use is made of Fe 4298 as the check line and the ratio I Fe 4303/I Fe 4298 as = 1.4 in the absence of neodymium.

When using Nd 4303, a spectrograph having a reasonably large dispersion should be used, otherwise interference from Ca 4302.527 may be encountered.

For other sensitive lines of the common rare earths which have been used for their analysis in minerals and rocks, see Strock (1936 b, appendix), van Tongeren (1938), and Mitchell (1948). General information on the most sensitive lines for all rare earth elements is given at the end of this book. In the main this information is based on the observations of Smith and Wiggins (1948).

For the spectrochemical analysis of all rare earth elements in rocks and soils, a chemical pre-enrichment procedure seems feasible. Thus Sahama and Vähätalo (1939) describe an enrichment procedure to be carried out prior to the x-ray spectrographic analysis of all the rare earth elements. In silicate minerals and rocks, an enrichment of rare earths is obtained by removing the silicon with hydrofluoric acid, concentrating the rare earths in the Al-Fe hydroxide precipitates, and making a final separation as oxalates. In place of the x-ray spectrographic analysis of the enrichment fraction, optical spectrochemical analysis could probably be used.

An enrichment procedure has been employed by De Rubies and Doetsch (1935) for the detection of very low concentrations of the rare earth elements in lead minerals, notably *pyromorphite*. Here selective volatilization may be used to build up a residue of the refractory elements, as described in Section 5–5. If *pyromorphite* is arced, and if the total duration of arcing is divided into three phases, the elements present in each phase are as given in Table 16–2. Specimens of mineral are arced until the end of the second phase, and when an appreciable residue is built up this is arced and the exposure is made. Whether or not such a procedure could be applied to silicate minerals, rocks, and soils is conjectural. Na, K, Si, Fe, Mg, Ca, and Al would first have to be volatilized. Difficulty might arise from the fact that the alumina bead is not easily arced and has a tendency to be ejected from the electrode cavity.

Table 16-2

Phase	Detectable elements														
1	P	As	Zn	Ag	Pb	V	Cr	Fe	?						
2	-	-	?	?	?	V	Cr	Fe	Mn	Be	Al	Y	La	Yb	
3	-	-	-	-	-	V	Cr	Fe	Mn	Be	Al	Y	La	Yb	Gd	Er

In an endeavor to obtain information about the spectrochemical analysis of a typically involatile element, Bauer (1935) chose lanthanum. Rare

earth elements are relatively involatile;* zirconium was used as an internal standard because it is very difficult to volatilize. A base of $CaCO_3$ was employed. When a standard was arced to completion, using cathode layer excitation, Bauer noted that the atom lines of lanthanum emitted their peak intensities early, that is, during the main period of calcium volatilization, whereas the ion lines were emitted with peak intensity after the bulk of material had volatilized. This is explained by the cooling influence of calcium (ionization potential 6.09 volts) during the early period of arcing, and a sharp increase in temperature and consequent greater degree of ionization after the calcium is distilled. This is one cause of the difficulty encountered in determining the most sensitive rare earth lines. These elements readily emit both atom and ion lines, but respective sensitivities vary considerably with changes in the energy of excitation. In general, however, the most sensitive lines of the rare earth elements in the arc are emitted by ions. Bauer found the use of a very small cathode, which held only 1.4–1.6 mg of specimen, most satisfactory.

For the analysis of the rare earth elements in rare earth minerals, McCarty, Scribner, Lawrenz, and Hopkins (1938) also used zirconium as an internal standard. An accuracy expressed as a maximum error of $\pm 15\%$ was reported. These authors made the significant suggestion that improved accuracy could probably be attained provided another rare earth element were used as the internal standard. This prediction is based on the knowledge that all the rare earth elements behave very similarly in the arc. All are relatively involatile, and many of their lines have similar excitation potentials. Cerium is suggested because it can be separated quantitatively from all the other rare earth elements with reasonable facility and may then be reintroduced in known amount.

Fassel (1949), who has utilized this suggestion, describes a method for the analysis of yttrium and gadolinium in rare earth mixtures over a very wide concentration range. One part sample is mixed with four parts CeO_2 and five parts graphite. High amperage (17 amp) anode excitation is employed and Fassel finds that over a long period of arcing the intensity ratio $\frac{I \text{ Y } 4358}{I \text{ Ce } 4339}$ remains very nearly constant. Since the lines have similar excitation potentials, a high reproducibility is expected. Fassel finds that for yttrium and gadolinium the standard deviation is about $\pm 2.5\%$ at most concentrations. This is an excellent example of how good a reproducibility is attainable when an ideal internal standard is used. One is quite frequently appalled at the choice of internal standards. Often

* Fassel (1950) has reported samarium as more volatile than the other rare earth elements.

enough, the main criterion seems merely to be the location of the internal standard line on the plate.

Instead of separating the internal standard (cerium) and then reintroducing it as 80% CeO_2, Fassel points out that it is possible to determine the concentration of ceria in the specimen and add the requisite amount. It seems, too, that the step of the addition of ceria might sometimes be omitted, because a variable internal standard procedure seems feasible (Section 7–4).

This work on the accurate analysis of the rare earth elements appears to have considerable potentialities for rare earth analyses in rare earth minerals. If the tedium of chemically fractionating the rare earths can be replaced by a rapid spectrochemical procedure capable of analyzing the rare earth elements with an accuracy (expressed as standard deviation) of about $\pm 2.5\%$, the spectrochemical method should be of much value. Further evidence of the efficacy of one rare earth element as an internal standard for the analysis of another is given by De Azcona (1941 b) and Fassel and Wilhelm (1948).

As the rare earths are transitional elements, they emit extremely complex spectra, and the analysis of the spectrum of a mineral rich in rare earths is often a spectrochemist's nightmare. When the rare earth elements enter the arc column, their oxidation causes the emission of intense continuous radiation and the extreme complexity of the spectra necessitates a spectrograph of very large dispersion. Many of the rare earths emit oxide band spectra in the visible spectrum and these may be used even if an instrument of small dispersion is employed. These bands are visually detectable in a spectroscope (Section 5–11). See also the observations of Piccardi (1939) on molecular emission of ScO, YO, LaO, GdO, SmO, and EuO. Piccardi employed a flame source, but many of these emitters develop in the arc as well (Section 5–11).

Additional references: Haberlandt (1939), Gatterer (1942), Selwood (1930), Borovik (1937), Borovik and Burova (1937), Borovik and Burova (1938), Gatterer and Junkes (1939), Milton, Murata, and Knechtel (1944), Wager and Mitchell (1943), Goldschmidt and Peters (1931 b).

CHAPTER 17

Sc; Zr AND Hf; U AND Th; Re

17–1. Scandium. Scandium is one of the most widely distributed of all the rarer elements. Like gallium, it can be detected spectrochemically in many minerals, rocks, and soils. Whereas gallium is associated with aluminum, however, scandium is ubiquitous in ferromagnesian (mafic) minerals. Here Sc^{+++} is octahedrally associated with Fe^{++} and Mg^{++} because its radius (0.83 A) is very similar to these two common cations, whose radii are 0.83 and 0.78 A respectively.

Scandium has several very sensitive lines, the most sensitive of which is the ion line Sc 4246. Using this line, concentrations of as little as 0.0001% of scandium, or even less, can usually be detected. This detection limit is considerably smaller than the concentration of scandium in many minerals, rocks, and soils.

The early writings of Eberhard (1908) mention the refractory behavior of scandium, as do those of Goldschmidt and Peters (1931 b). Because of this behavior, a relatively involatile internal standard should be used if an accurate analysis is to be made. Kvalheim and Strock (1939) used lanthanum, added as La_2O_3, as an internal standard and employed cathode layer excitation; standards were prepared as described in Section 7–20. An indication of the reproducibility for the analysis of scandium in *pyroxenite* is given in Table 17–1, which gives some of the results of Kvalheim and Strock. The analysis pair was Sc 4246:La 4263.

Table 17-1

	Kimberlite (So. Africa)		Olivine-biotite-pyroxenite (Canada)
	% Sc_2O_3		% Sc_2O_3
	0.0047		0.0092
	0.0047		0.0094
	0.0045		0.0100
	0.0060		0.0084
Av.	0.0050	Av.	0.0093

Because scandium does not enter minerals poor in iron and magnesium, feldspar has been used as a natural base material (Oftedal, 1943) in the preparation of standards for the analysis of scandium in silicates. Scandium was introduced into the base material as *thortveitite*, the only known scandium mineral.

Several other workers have determined scandium in minerals, rocks, and soils. Most of their pro-

cedures tend to be semiquantitative. Goldschmidt and Peters (1931 b) employed cathode layer excitation for their investigation of the geochemistry of scandium.

The general method of using palladium as an internal standard (Chapter 11) works reasonably well for scandium.

Additional references: Nockolds and Mitchell (1948), van Tongeren (1938), Borovik (1943 a), Borovik (1941), Sahama (1945 a and b).

17–2. Zirconium and hafnium. Zirconium is a commonly detected minor element in many rocks, minerals, and soils. Unlike most minor elements, which distribute themselves in suitable host minerals, zirconium occurs mainly as the mineral *zircon*. Nockolds and Mitchell (1948) discuss the distribution of zirconium in rock-forming minerals.

In all of its properties, hafnium is very similar to zirconium. So great is this similarity, in fact, that hafnium is almost completely masked by the more abundant zirconium in zirconium minerals. For this reason hafnium was not discovered until some 25 years ago. Hafnium, which is about 1/50 as abundant as zirconium, does not show very high spectral sensitivity and for this reason is not normally detectable in rocks and soils unless an enriched *zircon* fraction, or the pure mineral, is analyzed.

Zirconium is the most difficult of all elements to volatilize and an analysis for zirconium may be low because it has not been completely vaporized. If electrodes which have been used to arc a zirconium mineral supposedly to completion are re-arced, sensitive zirconium lines will probably appear with considerable intensity. This difficulty of volatilization may be due in part to the formation of ZrO_2. Strock (1941) has shown ZrO_2 as particularly difficult to vaporize. Its release from the electrode is probably further impeded by reduction to ZrC.* When molten, ZrC dissolves Zr and can change to ZrN, which has still greater stability. For most elements, the addition of powdered carbon tends to smooth out selective volatilization differences and subdue sharp volatilization peaks, but for zirconium such addition of powdered carbon has only a relatively small effect. Fig. 17–1 shows some selective volatilization curves of typically refractory elements, (A) without carbon admixture, and (B) after admixture with two parts of carbon. Of all the elements, zirconium is least affected by the presence of carbon. Anode excitation (7 amp) was employed for a specimen having a composition similar to granite. Experimental data are those of Mrs. L. G. Gorfinkle of the Cabot Spectrographic Laboratory, M. I. T.

This involatility of zirconium makes the choice of an internal standard for its accurate analysis critical. Refractory elements should be used.

* An x-ray examination of a zirconium rich residue in an electrode has shown the structure to be that of ZrC.

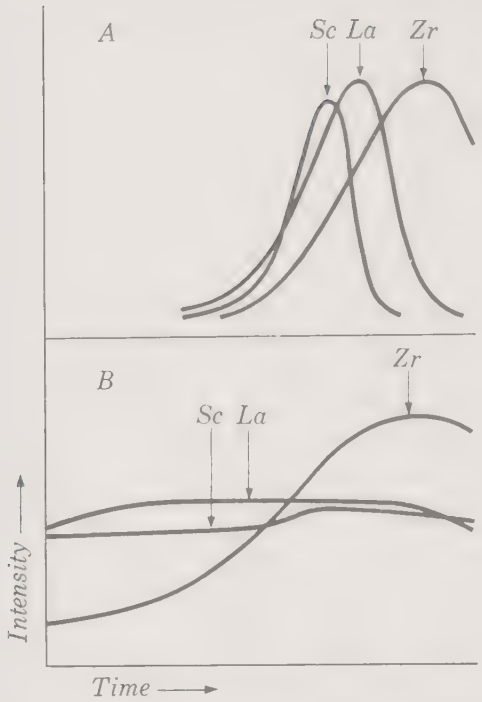


Fig. 17–1. Some typical volatilization curves for Sc, La, and Zr, (*A*) without addition of carbon and (*B*) with carbon admixture. Although the presence of carbon is usually successful in smoothing out volatilization differences, it is not very effective for Zr.

Apart from possible difficulties arising from its refractory behavior, zirconium can in general be conveniently analyzed. Its most sensitive lines are ion lines. Using Zr 3438 and Zr 3391, both of which are of convenient wavelength, a detection limit of about 0.001% zirconium is usually attainable.

Most published analyses of zirconium in minerals, rocks, and soils tend to be semiquantitative, but those of Bray (1942), who used palladium as an internal standard, are probably reasonably precise. The use of palladium and the general method in Chapter 11 has been found very satisfactory; see Table 11–2 for reproducibility data.

The analysis of hafnium in zircons has been described by Morgan and Auer (1941). Zirconium was employed as the internal standard, and the intensity ratio $\frac{\text{Hf } 3070}{\text{Zr } 3106}$ was used as a measure of the variation of hafnium in zircons. No standards were used and no abundance measurements were made. Zirconium is probably the most suitable internal standard for hafnium. However, there is considerable difficulty in obtaining zirconium salts which are free from hafnium.

De Rubies and Aguado (1935) have investigated methods for the analysis of hafnium. They describe the use of molybdenum as an internal standard. Several homologous line pairs are also given.

Evidently a detection limit better than about 0.01% is not easily attainable for hafnium. Although this limit does not enable the analyst to determine hafnium in the common minerals, rocks, and soils, the combined use of a chemical concentration and a spectrochemical procedure seems quite feasible. Thus hafnium in rocks has been determined by x-ray spectrography after a chemical enrichment with phenylarsonic acid, which precipitates Zr, Nb, Ta, and also Hf (Rankama, 1944). The concentration of hafnium in the precipitate is sufficient for spectrochemical analysis. The

sensitive lines of hafnium are discussed in the wavelength tables at the end of this book.

Additional references: Wager and Mitchell (1943), van Tongeren (1938), Norman and Johnson (1945), Kennard and Howell (1936), Strock and Drexler (1941).

17–3. Uranium and thorium. As a result of the discovery of nuclear fission, interest in the distribution of uranium and thorium in the earth's crust has been stimulated and speculation on the feasibility of rapid spectrochemical analysis for these two elements in possible source materials has been rife. Uranium and thorium are not very rare, but because of their relatively poor spectral sensitivities they are not directly detectable in common minerals, rocks, and soils. The detection limit for these elements under favorable conditions is approximately 0.01%. In rocks, a high proportion of these radioactive elements is found in *titanite* (*sphene*), *apatite*, *monazite*, and *zircon*.

More attention has been given to uranium than to thorium. Its spectrum is extremely complex and because no lines show high transition probabilities, the emitted radiant energy is dissipated among many lines. As a consequence, sensitivity is low. When present in high concentrations, uranium emits an intense continuous background radiation.

Early observations on the spectrochemistry of uranium were made by Porlezza and Donati (1926), who in the first of a series of investigations on the analysis of the different elements (see *Ann. chim. applicata* from 1924 on) found a limit of detection of 0.005% U_3O_8 in a silica base. In other bases sensitivity was much poorer. Some attempt at quantitative analysis was made, and results of analyses of *carnotite* are given. Porlezza and Donati reported U 4241.669 as the most sensitive line, and later workers are in accord with this observation. *Zircon* may carry appreciable traces of uranium, but here there is interference from Zr 4241.687.

Currah, Beamish, Allen, and Bartlet (1945) determined uranium in MnO_2 and used silver electrodes and a 4-amp arc. U 4090 and 4543 were the analysis lines. Mather (1947 a) found a lower limit of detection for cathode layer excitation than for anode excitation. This has not been the experience of other observers, who have found anode excitation slightly superior.

Mather gives 124 sensitive uranium lines and lists 5008.22, 4362.26, 4244.37, and 4042.75 as the most suitable for determining uranium in iron-rich specimens. For the analysis of uranium as metal, Steadman (1948) used U 2882.7, 2882.6, and 2882.9 as the analysis lines and platinum as the internal standard.

Uranium is very involatile, and the use of a relatively involatile internal standard is indicated. In uranium-rich minerals (*uraninite* for example), a rare earth element or thorium (added in excess if necessary, to offset thorium already present) may be used as an internal standard. A high dilution in carbon powder, and the use of a small anode and high amperage are recommended for highest precision. The general method (palladium as internal standard) outlined in Chapter 11 may be used for uranium down to concentrations of about 0.1%.

Strasheim (1950) has investigated the analysis of uranium in ores in some detail. For concentrations within the range of 0.1%–6.0% U_3O_8 direct arcing (anode excitation) of the specimen is used, after mixing 9:1 with graphite powder. Vanadium, as V_2O_5 is the internal standard and U 4244:V 4232, the analysis pair. A standard deviation of about 5% is attainable. Because of interference from a coincident iron line,* the sensitive U 4241.669 line was not used.

Table 17–2 compares spectrochemical values with those obtained by other methods; agreement is very good.

In a second procedure described by Strasheim, 1:1 dilution with $PbCl_2$ replaces 9:1 graphite-to-specimen dilution. Using a somewhat larger quantity of specimen, a detection limit of 0.006% U_3O_8 may be reached. As before, vanadium is the internal standard and an accuracy similar to that indicated in Table 17–2 is apparently attainable over the range 0.006%–1.3% U_3O_8.

A third procedure involves extraction with CH_3COOH (100 parts) + HNO_3 (5 parts). Iron, which is extracted at the same time, is estimated in the extract, adjusted to constant concentration by further addition of iron, and used as the internal standard. Several iron lines serve as internal standard lines for U 4241 and U 4244. Although there is interference with U 4241, it is not excessive and it is constant; as a result U 4241 may be used.

In a Spectrographer's News Letter (1949), several sensitive uranium and thorium lines are listed.

Table 17-2

Sample No.		% U_3O_8 Chemical	Counter	Spectrochemical
1		. . . .	0.10	0.10
2	(American Standard)	0.16	. . . .	0.165
3		0.22	. . . .	0.252
4		. . . .	0.207	0.20
5		0.25	. . .	0.24

* The interfering iron line is not listed in the M.I.T. tables.

The spectrochemistry of thorium is very imperfectly known. Like uranium, it is very involatile. In minerals, rocks, and soils, thorium can be concentrated chemically in the rare earth oxalate fraction (Sahama and Vähätalo, 1939). The x-ray spectrograph was used to analyze thorium in this enriched fraction, but the use of optical spectrochemical analysis is entirely feasible. Zirconium has been used as an internal standard for thorium (Murata, 1950). This appears to be a logical choice.

Additional reference: (Uranium). Mercader and Benavente (1949).

17–4. Rhenium. This extremely rare element cannot be detected spectrochemically in rocks, soils, and most minerals. It is geochemically associated with molybdenum, and in *molybdenite* the concentration of rhenium is sometimes sufficient for its spectrochemical analysis. In *molybdenite*, rhenium concentration may reach a maximum of 0.1% (Geilmann, Lange, and Barttlingck, 1945–48). Borovik and Gudris (1936) examined the sensitivity of rhenium by cathode layer excitation in molybdenum and *calcite* matrices. At 0.01% rhenium, Re 3464 and Re 3460 could be detected. The spectrochemical analysis for rhenium has also been discussed by Hurd (1936).

Additional reference: Kimura and Koyama (1936).

CHAPTER 18

THE NOBLE METALS
Ag; Au; Pt, Pd, Rh, Ir, Os, AND Ru

18–1. Silver. Silver has a very high spectrochemical sensitivity (limit of detection, 0.0001–0.00003%). This, however, is not usually quite sufficient for its spectrochemical detection in most common rocks and common silicate minerals, because its abundance in the earth's crust, expressed as weight-per cent, is about 0.00001%. In many rocks, however, the silver concentration hovers near its detection limit and in basic types silver is sometimes detectable; it is also sometimes detectable in soils. In sulfide minerals (*galena*, *sphalerite*, and *pyrite* for example), it is frequently detectable and is often sought there spectrochemically.

The two most sensitive lines of silver, Ag 3280 and 3383, are conveniently placed. Interference is not common, but in the presence of significant traces of manganese, as in manganese-rich *sphalerite*, interference from Mn 3280.756 with Ag 3280.683 may be encountered. Silver is relatively volatile in the arc, and such interference can be reduced by using low amperage excitation and recording only the early period of arcing.

Marks and Potter (1948) have employed the general "total energy" procedure outlined in Chapter 11 for the determination of silver in ores. Some reproducibility data are given in Chapter 11. An investigation of the effect of varying matrix composition on line intensity showed that in the presence of much Fe, Co, and Ni, both Ag 3280 and 3382 were unusually weak. The possibility that collisions of the second kind are a cause of this weakening has been discussed. Combined sulfur was found to exert only a very slight effect on line intensity, whereas sulfur in elemental form caused a marked weakening. A $CaCO_3$:graphite mixture was used effectively as a buffer against effects of compositional changes.

In the Cabot Spectrographic Laboratory, M. I. T., indium has been used as an internal standard for the analysis of silver in some of the more basic rock types in which it is sometimes detectable. The line pair Ag 3280: In 3256 is the analysis pair, and the general procedure is referred to in Chapter 11.

By means of fire assay procedures (Section 18–2), silver can be concentrated in minerals, rocks, and soils, and a spectrochemical analysis may then be made of this concentrate.

Additional references: Oftedal (1941), Frondel, Newhouse, and Jarrell (1942), Rost (1939), Evrard (1945), Lunde (1927), Lunde and Johnson-Høst (1928), Claussen (1934).

18–2. Gold. Gold is considerably rarer than silver and cannot be detected spectrochemically in rocks, soils, and most minerals. Even in so-called gold ore, the gold concentration may be below its limit of detection, which is about 0.001%.

The standard procedure for the analysis of gold is by fire assay. The main steps in this procedure are as follows. First, the specimen is fused with a suitable alkali-flux mixture (K + Na carbonate + borax + suitable Pb compound) from which a lead *button* is obtained. This is then cupelled to drive off relatively volatile lead. A residual bead, the doré bead, is left. In this bead are concentrated Au, Ag, Pt, Pd, Rh, Ir, Os, and Ru. In fire assay analysis, the *doré* bead is further treated (parted) and a pure gold bead is obtained and weighed. If a spectrochemical analysis is to be attempted, the step of parting is omitted. Scobie (1945) has described such a combined fire assay-spectrochemical analysis procedure for the analysis of gold when it is present at very low concentrations. At these extremely low concentrations normal fire assay procedures are not accurate because of the small weight of the gold bead. Scobie employed an a.c. arc, but probably a d.c. arc could also be used. Scobie reports that this combined procedure is faster, more sensitive and, at very low gold concentrations, more accurate than fire assay alone. The ability to analyze for the platinoids (Section 18–3) is an added attraction.

Hegemann and Rost (1937) describe the necessary steps for the analysis of gold in *pyrite*. They point out that because of the very inhomogeneous distribution of gold in pyrite, careful attention must be given to sampling and the use of at least 100 gm of sample is recommended. The roasted mineral is attacked with mineral acids and a *doré* bead is prepared from the evaporated residue in the usual manner. This bead is then spectrochemically analyzed.

Gold has also been concentrated by the use of an NaCN extraction which is electrolyzed (De Azcona and Pardo, 1942). The cathode is a carbon rod which contains a mercury droplet in a cavity at the upper end. After electrolysis, the same electrode is used for spectrochemical analysis.

In many gold ores, the gangue is highly siliceous. If an attempt is made to determine gold spectrochemically, interference from SiO bands (Section 10–2) will be encountered unless their emission is quenched. Thus, Ahrens and Liebenberg (1946) found the band with head at 2413 A interfered considerably with Au 2428, the most sensitive gold line. The next most sensitive gold line, Au 2676, also had interference from SiO bands, but this was less marked. However, gold is relatively volatile, and is more volatile than silicon. To accentuate this difference, low amperage anode excitation was employed and only the first thirty seconds of arcing was exposed. Sensitivity was improved by a factor of about 5–10, and 0.003% gold

could easily be detected in such highly siliceous material as the gold bearing *banket* of the Witwatersrand (S. Africa). The efficacy of this technique can best be observed by an examination of the spectrograms given by Ahrens and Liebenberg (1946). The highest sensitivity could probably be attained by carrying out the analysis in an atmosphere free from oxygen, which should remove SiO emission almost completely (Section 10–2).

In a procedure described by Toisi (1940), about 0.35 gm of powdered specimen is allowed to fall from above onto inclined electrodes for ten seconds. Using a 10-amp arc, the limit of detection is near 0.001%. Toisi claims a high quantitative reproducibility for this method.

Additional references: Nedler (1941), Nedler and Efendiev (1941), Peters (1933), Iwamura (1932 b) Pardo (1941), Lunde (1927), Lunde and Johnson-Høst (1928).

18–3. Elements of the platinum group (Pt, Pd, Rh, Ir, Os, and Ru). The elements of the platinum group are of extreme rarity and cannot be detected spectrochemically in rocks, soils, or most minerals unless some preliminary concentration has been made. Like gold, these elements are almost invariably found native because of their nobility or characteristic inertness. On occasion, however, they may be present in combined form, associated with sulfide minerals. In general, the platinum group of elements concentrates in very basic rock types in quantities well below spectrochemical detection.

The general geochemistry of these elements has been studied by Goldschmidt and Peters (1932 b) who employed a combined fire assay-spectrochemical procedure like that for gold (Section 18–2). For this purpose about 0.5 gm of sample was used; these authors employed cathode layer excitation of the *doré* bead. The general procedure of fire assay enrichment and spectrochemical analysis is further discussed by Peters (1933), who points out the necessity for terminating cupellation before all lead has been driven off. Otherwise, relatively volatile OsO_4 and RuO_4 may in part be lost. Peters (1933) also used cathode layer excitation of the *doré* bead and

Table 18-1

Arcing interval	Elements showing spectra								
0-20 sec	Pb	Ag							
25-45 "	Pb	Ag	Au						
50-70 "	-	Ag	Au	Pd					
75-95 "	-	-	-	Pd	Ru	Rh	Pt		
100-120 "	-	-	-	Pd	Ru	Rh	Pt	Ir	
125-145 "	-	-	-	-	Ru	Rh	Pt	Ir	Os
150-170 "	-	-	-	-	-	Rh	Pt	Ir	Os

employed the following as the most sensitive lines: Pt 2659, Pd 3242 and 3404, Rh 3434, Ir 3220 and 2924, Os 3058, and Ru 3436. When the *doré* bead was arced to completion and spectra were recorded at given intervals, the elements were found to volatilize selectively as shown in Table 18–1.

Elements of the platinum group are thus seen to be less volatile than silver or gold, and in general they may be regarded as involatile. According to Goldschmidt and Peters (1932 b) the sensitivities of elements of the platinum group vary considerably. They give these detection limits:

Ru, Rh and Pd:	0.001%
Pt:	0.005%
Ir and Os:	0.01%

Scobie (1945) and Pardo (1941) have also employed combined fire assay-spectrochemical analysis methods and stress the advantage of the fact that the analysis of gold and each of the platinum group elements can be carried out in a single operation.

On rare occasions it is possible to detect platinum and a few of the other noble elements in certain mineral types without the necessity of preliminary concentration. Thus Schneiderhöhn (1929) investigated the distribution of the platinum group elements in some of the rocks of the Bushveld Igneous Complex (Transvaal). Sparsely distributed sulfide minerals were isolated and spectrochemical analysis showed *pyrrhotite*, *pentlandite*, and *nickeliferous pyrite* to be the host minerals for Pt, Pd, Ir, Rh, Ru, and traces of Os. All other minerals were barren of these elements. This is an effective and elegant example of the combined application of a knowledge of geology, microsampling, and spectrochemical analysis.

Without attempting any concentration, Ahrens and Liebenberg (1946) reported the presence of platinum in some basic rocks from the Bushveld Complex. Pt 3064.712 was used. The apparent presence of platinum, since shown to be in error, was due to interference from Ni 3064.623. Using direct spectrochemical analysis, Chapman and Schweitzer (1947) have reported the presence of Pt, Ir, Ru, and Rh in granitelike rocks from New Hampshire. In view of the extreme rarity of these elements in rocks, these findings are difficult to accept.

Additional references: Schneiderhöhn and Moritz (1939), De Azcona and Pardo (1942).

CHAPTER 19

W; Mo; Nb AND Ta; Te AND Se; P

19–1. Wolfram. Wolfram is relatively rare. In many common rock types its concentration is of the magnitude of 0.0001–0.0002%. This is below the limit of detection of spectrochemical analysis, and consequently wolfram is not reported in the routine analysis of rocks, soils, and most minerals.

Combined chemical concentration and spectrochemical analysis can be used for the determination of these low concentrations of wolfram. Wilson and Fieldes (1944) treated their powdered rock specimens with $HF + H_2SO_4$. Once in solution, wolfram was collected on a carrier precipitate of titanium developed by the addition of tannin, antipyrine (phenazone), and cinchonine. A spectrochemical analysis of the ignited precipitate was made after its admixture with ammonium sulphate. Using W 2948, a detection limit of 0.00007% wolfram was reported.

An enrichment procedure for the analysis of wolfram in classifier sands has been described by Scobie (1943). A hydrated alumina precipitate which acted as a collector for wolfram was obtained from a solution. Using W 2896, a concentration as low as 0.0002% was detected.

A sensitivity better than that usually recorded has been reported by Kaufman and Derderian (1948), who were able to detect as little as 0.0005% wolfram using W 4294, without concentration. The method was developed for the analysis of low-grade wolfram ores (0.001–0.3% WO_3). Each specimen was mixed with one or two parts of AgCl, which served to volatilize wolfram very quickly. Thirty seconds were found sufficient to vaporize all wolfram, using anode excitation. A relatively low limit of detection (0.001% W) has also been reported by Sergeev (1947), who employed a rather novel procedure. Carbon electrodes were mounted horizontally 0.5 mm above the powdered specimen. When the arc was started, the rock powder melted, and a magnet placed 15–20 mm above the arc axis caused the vapor to diffuse upward and become excited. Sergeev claims that the resultant spectra are relatively free from background.

Although wolfram metal and wolfram carbide are very refractory, wolfram in low concentration is usually fairly volatile in the arcing of minerals because of the formation of WO_3, which sublimes quite easily. This fact enabled Ahrens (1943 b) to use silicon, an element of medium volatility, as an internal standard for the analysis of wolfram in highly siliceous ores. Using 6–7 amp anode excitation, a standard deviation

of ±6% could be attained. In highly siliceous materials, emission of SiO bands interferes considerably with several sensitive wolfram lines (Ahrens, 1943 b). Cobalt and nickel, two other elements of medium volatility, have been used as internal standards for the analysis of wolfram in ores. Raikhbaum (1939) used cobalt and noted that volatilization of cobalt and wolfram was depressed in the presence of NaCl. Nedler (1940) used nickel. Both authors investigated the behavior of the intensity ratio of the analysis pair when specimen composition changed.

W 4008.753 has been used by Brintzinger and Titzmann (1948) for the analysis of wolfram (up to 2.2%) in slags. Reference is made to interference from Ti 4008.928 and the necessity for using a spectrograph of large dispersion.

Additional references: Donati (1927), Ratsbaum (1936), Mitchell (1948, p. 117), Carlsson (1943).

19–2. Molybdenum. Unlike wolfram, molybdenum is quite frequently reported in the spectrochemical analysis of common rock types and also soils, although its concentration often borders on the detection limit. The detectability of molybdenum therefore depends to a large extent on the sensitivity of the particular spectrochemical procedure employed. Nockolds and Mitchell (1948) have shown that in rocks, molybdenum concentrates in *sphene* (*titanite*).

Unfortunately, the two most sensitive molybdenum lines, Mo 3798 and Mo 3902, can rarely be used because of interference. The CN band with head at 3883 A interferes with Mo 3798, and Fe 3902.946, a very intense line of iron, interferes with Mo 3902.963. However, Mo 3170 is relatively sensitive and generally free from interference. Using this line, Mitchell (1948) reports a limit of detection as low as 0.0001%. This sensitivity was sufficient for Wager and Mitchell (1943) and Nockolds and Mitchell (1948) to determine molybdenum in rocks and separated minerals. Cathode layer excitation and visual estimations were made as described in Chapter 11. It seems feasible that if CN emission were eliminated (Section 10–2), Mo 3798 could be employed. Its use would probably enable analysts to determine lower concentrations of molybdenum than has hitherto been possible.

Borovik (1943 c) describes a method for the analysis of molybdenum, using chromium and platinum as internal standards. A spectrochemical method for the analysis of molybdenum and wolfram in ores is described by Carlsson (1943). A copper electrode is used and each specimen is mixed with FeO and a salt of potassium prior to arcing.

In rocks and soils where the molybdenum concentration is below detection, a chemical enrichment procedure may be employed (Chapter 11).

Like tungsten, molybdenum forms a stable trioxide, MoO_3, which readily sublimes and accounts for the relative ease with which molybdenum volatilizes from rocks and minerals.

Additional reference: Preuss (1937).

19–3. Niobium and tantalum. Neither niobium nor tantalum is usually reported in the routine spectrochemical analysis of rocks, soils, and most common rock-forming minerals. However, niobium is frequently present in a wide variety of mineral, rock, and soil types, in concentrations which border on and quite often exceed its limit of spectral detection, which is about 0.001%. In granitelike rocks and in syenites (particularly in nepheline syenites), niobium is often detectable. The radius of Nb^{+++++} (0.69 A) causes it to enter minerals which offer octahedral structure sites (*mica*, for example). In general, it is associated with titanium and is easily detectable in many titanium minerals. Deep-sea ocean sediments frequently contain detectable amounts of niobium as well. Rankama (1948) gives detailed information on the distribution of niobium and its abundance in the earth's crust.

The geochemistry of tantalum is given in detail by Rankama (1944). In general, however, this element is not spectrochemically detectable in common minerals, rocks, and soils. Tantalum is very closely associated with niobium, but is less abundant (by a factor of about 10, according to Rankama, 1948) and has a much poorer spectral sensitivity. Whereas some spectrochemists have placed the detection limit at about 0.1–0.3%, Standen (1944) reports a detection limit of 0.01%, using Ta 2714. Likewise, Harrison (1949) also finds a reasonably good sensitivity for tantalum. The reason for the considerable disparity in sensitivities is not readily apparent.

Nb 4058 and 4079 are the two most sensitive lines of niobium; Nb 4058 is more sensitive than Nb 4079. In addition to interference sometimes encountered from the CN band with head at 4216 A, there may be line interference. Both lines may have interference from manganese lines. Mn 4058.930 may interfere with Nb 4058.938, and Mn 4079.422 with Nb 4079.729. These manganese lines are quite often detectable in basic rock types. Rankama and Joensuu (1946) mention occasional interference of Fe 4058.760 and Zr 4058.624 with Nb 4058. Provided the concentration of niobium is about 0.01% or more, less sensitive niobium lines situated in the ultraviolet may be used.

For his investigation on the geochemistry of niobium and tantalum, Rankama frequently employed a chemical enrichment procedure. About 10 gm of specimen was attacked with $HF + H_2SO_4$. Phenylarsonic, tartaric, and salicylic acids were used to effect the necessary concentration

of niobium and tantalum. The ignited residue of the final precipitate was then analyzed. For niobium a spectrochemical procedure was employed, as described by Rankama and Joensuu (1946). Each specimen was diluted with TiO_2 and mixed with 4 parts carbon powder and 1 part NaCl. Using cathode layer excitation and Nb 4058, a lower limit of 0.001% Nb could be detected.

For the analysis of tantalum in the enriched residue, Rankama (1944) employed the x-ray spectrograph. It seems feasible that spectrochemical analysis could be employed on the enriched product.

A few spectrochemical determinations of niobium in rocks have been made without chemical pre-enrichment, notably those of Sahama (1945 a) and Goldschmidt (1937 b; analyst Bauer).

Because of the increasing importance of niobium and tantalum in metallurgy there has lately been much prospecting for their ores, especially *columbite-tantalite*. The need has arisen for a rapid and accurate determination of niobium and tantalum (the earth acids). Chemical methods can isolate a mixture of earth acid oxides ($Nb_2O_5 + Ta_2O_5$) with reasonable speed and facility, but the analysis of the individual earth acids thereafter is most difficult and tedious. An attempt has therefore been made to analyze niobium and tantalum in ores after a preliminary chemical separation of the mixed oxides. Such a method has been described by Herman (1948). The chemical separation of the earth oxides is made in accordance with the directions given by Schoeller (1937).

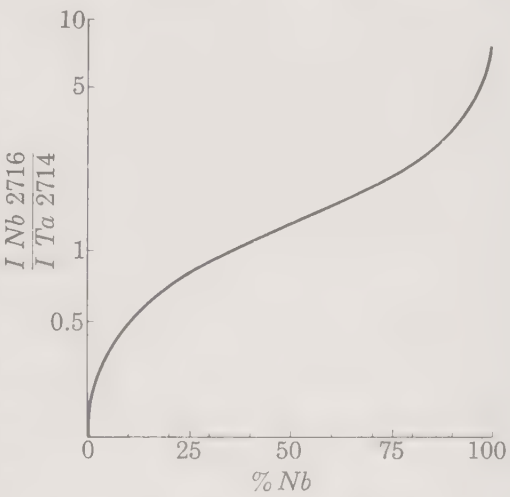


Fig. 19–1. Working curve for niobium in a two-component mixture of Nb_2O_5 and Ta_2O_5.

For the mixed oxides, variable internal standardization is used. Such a step is logical because the properties of niobium and tantalum are similar in the arc; both elements are relatively involatile. Fig. 19–1 shows a working curve which is a plot of %Nb vs $\log \frac{I\ \text{Nb}\ 2716.624}{I\ \text{Ta}\ 2714.674}$. The shape of this curve (when plotted this way) is typical of that produced by the use of variable internal standardization in what is essentially a bicomponent mixture. Small amounts of titanium, wolfram, and a few other elements may be present in the mixed oxides, but they cause no disturbance of line intensities.

Using a 10-amp arc and cathode excitation, an excellent reproducibility is claimed.

Additional references: Breckpot (1938), Breckpot and Creffier (1937), Creffier (1938), Carobbi and Pieruccini (1941), Jaffe (1947).

19–4. Tellurium and selenium. Tellurium probably shows the highest arc sensitivity of all elements of the sulfur group. In common minerals, and in all rocks and soils, the tellurium concentration is far below its limit of detection, which is about 0.01%. Tellurium is sometimes sought spectrochemically in a few relatively rare minerals.

The arc spectrum of tellurium is extremely simple. The analyst has only two sensitive lines, Te 2383 and 2385, from which to choose. Te 2142 is theoretically the most sensitive tellurium line, but its wavelength is just outside the normally usable range. If tellurium is sought in an iron-rich gangue, Fe 2383.24 will interfere with Te 2383.25 (Ahrens and Liebenberg, 1946). These authors show how the difference in volatility of iron and tellurium can be used to minimize this interference. Te 2385 should usually be used, however, because it appears to be freer from interference and is a more sensitive line.

Selenium has commonly been classified with the relatively insensitive elements in the arc. However, Feldman (1945) has been able to detect selenium at concentrations as low as 0.01% under certain conditions. He found that the intensity of Se 2413 was markedly enhanced by the addition of 10% tellurium to the specimen, which was a CuSe-CuS mixture; this enabled him to reach this unusually low concentration. In a base of MgO, KCl, or $CaSO_4$, the presence of tellurium is ineffective for enhancing sensitivity. Feldman suggests a concentration method for Se (and Sb, As, and Hg) in which these elements are sublimated in a hard glass tube. Here the sublimate is collected in a molten pellet of tellurium which is brought into contact with the wall surface. The pellet is then analyzed.

Both selenium and tellurium are very volatile.

Additional references: Mitchell (1948, pp. 115–116), Milbourn (1937).

19–5. Phosphorus. Phosphorus is widely distributed in many minerals, rocks, and soils, where concentrations of about 0.1% are quite common. However, it is very rarely reported spectrochemically in these materials. P 1774 is theoretically the most sensitive line of phosphorus but P 2535.65 is the most sensitive usable line. However, interference from Fe 2535.604 makes P 2535 impractical for minerals, rocks, and soils, and P 2553, the next most sensitive line, must be used here.

Even when P 2535 is usable, phosphorus is not usually regarded as very sensitive. A detection limit of about 0.01% seems reasonable (see Standen,

1944, for example), although Norman and Johnson (1945) report a considerably higher sensitivity.

In the arc, band spectra are emitted from PO, the most sensitive heads of which are located at 3255.3 and 3270.5 A. These bands are not sensitive, however, and usually they are not detectable at concentrations less than 0.5–1.0% P. They are of a convenient wavelength and may be used to ascertain whether or not phosphorus is a major component in a mineral. The frontispiece shows PO bands as emitted from a specimen of *monazite*. Phosphorus is relatively volatile, and only the early period of arcing need be recorded. If later arcing periods are used in the analysis of monazite, PO bands become smothered by a mass of cerium earth and thorium lines which are emitted intensely only at later stages of the arcing period.

Additional reference: Mitchell (1948, pp. 113–114).

CHAPTER 20

Zn, Cd, As, Sb, Bi, AND Hg

If standard spectrochemical procedures are used, it is rarely possible to detect these elements in common silicate minerals, rocks, and soils. Zinc is an exception because it is quite often detectable in such iron-rich minerals as *magnetite* and *biotite* and sometimes in *muscovite*. Zn^{++} is an ion of medium size (radius 0.83 A) and enters many minerals octahedrally. Since the radius of Fe^{++} = 0.83 A, Zn^{++} readily substitutes for Fe^{++}. None of the elements of this group is extremely rare, and all of them may frequently be detected in many sulfide minerals. Because zinc is easily accepted in sulfide and silicate minerals, it exhibits dual geochemical properties, like those of Ga, In, Tl, and some other elements.

Ease of volatilization is characteristic of the elements of this group and mercury is probably the most volatile of all elements sought with the arc. Highest sensitivity is attainable when a deep electrode cavity is used, irrespective of whether anode, cathode, or cathode layer excitation is used. For mercury, Myers and Brunstetter (1939) describe an electrode cavity 15 mm in depth. The diameter of this cavity (6.4 mm) was also unusually large. Because of the high volatility of these elements, the furnace technique of Preuss and others (Section 5–5) may be applied very successfully. Through its use, sensitivity can be very considerably enhanced and the operator can detect and estimate Sb, Bi, Cd, and Hg in many rocks and soils without any chemical concentration. See also National Carbon Company (1949) for mercury.

One of the common host minerals for several elements of this group is *sphalerite*. Oftedal (1941) employed cathode layer excitation for the analysis of sphalerite and galena. He observed that whereas *galena* and iron-poor *sphalerite* could be successfully arced to completion without admixture with any element or compound, iron-rich *sphalerite* formed a residual iron-rich bead which was invariably ejected. Consequently, each specimen was mixed 1:1 with carbon powder. Zinc was sometimes used as an internal standard for quantitative analysis.

For cadmium, the line pair Cd 3261:Zn 3282 was employed and a very good reproducibility was obtained (most determinations within $\pm 5.0\%$ of correct amount). Here we have an example of the successful use of two atom lines which, however, have very different excitation potentials: Cd 3261 = 3.78 volts, Zn 3282 = 7.75 volts, and Δ volts = 4.0. Zinc and cadmium are both very volatile, and arc temperature was buffered by the

presence of sodium vapor from feldspar (see below). As a result, the intensity ratio of the analysis pair was not easily disturbed. *Albite* was added to improve the burning characteristics of the arc, but for the analysis of some constituents (gallium, for example) NaCl was used. Both albite and NaCl introduce sodium vapor into the arc, but the intensity ratio $\frac{\text{Cd } 3261}{\text{Zn } 3282}$ was found to differ considerably in the two sodium sources. This is shown in Fig. 20–1 (adapted from Oftedal's paper), which gives plots of $\frac{I \text{ Cd } 3261}{I \text{ Zn } 3282}$ vs % Cd, one with addition of albite and one with addition of NaCl. Evidently the anion plays an important role here in influencing intensity ratio.

Cd 2288 is the most sensitive line of cadmium, but because it is inconveniently placed in the far ultraviolet it is not commonly used. Plates sensitized to the ultraviolet are necessary. Usually Cd 3261, the next most sensitive line, is employed and with this line a detection limit of about 0.001% can be reached.

For the analysis of cadmium in ores, Marks and Jones (1948) have used the general procedure outlined in Chapter 11 (Marks and co-workers). Rusanov and Alekseeva (1945) employed antimony as an internal standard for cadmium in sulfide minerals. Using the line pair Cd 3261 : Sb 3232, a probable error of ±10% is reported. The presence of lead was found to weaken antimony lines. This was explained by postulating absorption of antimony by lead in undecomposed particles of lead ore.

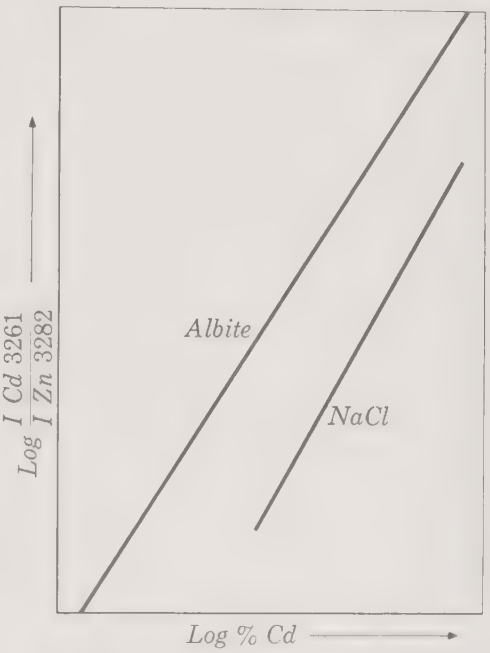


Fig. 20–1. Two working curves for the analysis pair Cd 3261 and Zn 3282, one in the presence of albite and the other in the presence of NaCl. The anion has apparently been the cause of the change in intensity ratio.

Mercury is occasionally detectable in some sulfide minerals, such as *sphalerite*. Hg 2536 is the most sensitive line, and Oftedal (1941) reports a detection limit as low as 0.001% in sphalerite. This is lower than is usually reported, and Oftedal points out that this sensitivity was observable only when the mercury was held within the mineral structure, as in sphaler-

ite. In synthetic standards of like composition, the detection limit was about 0.01%. This is an example of extreme changes of sensitivity in matrices of like chemical composition but different physical structure. Strock (1945) reports a detection limit of about 0.01%. He and Oftedal caution against the use of Hg 2536 in sulfide minerals because of possible interference from Co 2536.493, which becomes apparent at concentrations of about 0.1–0.2% Co. Strock employed cathode excitation and mixed each specimen with four parts of carbon powder and one part of buffer-internal standard mixture (NaCl + 0.1% BeO). Buffering by NaCl produced conditions conducive to the maximum intensity of emission of gallium and indium lines (thallium would be influenced in the same way), but depressed line intensities of lines of Cd, Sb, Hg, and possibly Bi. Lines of Zn, As, and probably Ge and Sn are often depressed by the presence of alkali metal vapor in the arc as well.

Strock employed two cathode sizes, one relatively small (3 mm ext. diam. × 1/16″ int. diam. × 4 mm depth) and the other somewhat larger (7/16″ int. diam. and 5 mm depth). The larger electrodes were used for the detection and estimation of low concentrations, but were often unusable at high concentrations because of the incidence of self-absorption. Strock observed that the working curves for small and large electrodes were not superimposed (see comments in Section 15–1).

For an investigation on the geochemistry of arsenic, particularly in iron ores, Goldschmidt and Peters (1934) employed a spectrochemical procedure. In sedimentary iron ores, arsenic, by adsorption on colloidal $Fe(OH)_3$, evidently concentrates sufficiently for spectrochemical detection. Cathode layer excitation was employed, and each sample of iron ore was mixed with one part SiO_2 to prevent ejection of the iron-rich globule. Some sulfide minerals were also analyzed for arsenic. To ensure a satisfactory arc burn, they were first oxidized with HNO_3 and taken to dryness; then the dried residue was mixed with one part of SiO_2 and arced. The spectrochemical sensitivity of arsenic is not very high, and the lower limit of detection is usually about 0.01%. Either As 2780 or 2860 is usually used. As 2349 is more sensitive, but Goldschmidt and Peters did not employ it because they observed interference from band spectra. As 1890 is the most sensitive arsenic line, but because of its extremely short wavelength it is not normally used. Lines of arsenic show negligible cathode layer enrichment because of the high (10.0 volts) ionization potential.

Antimony is somewhat more sensitive than arsenic. Using Sb 2598, a detection limit of about 0.001% is attainable. Like other elements of high ionization potential (Te, Se, As, and Zn, for example), the most sensitive antimony line, Sb 2068, is placed far in the ultraviolet and is normally not used.

Veselovskii (1941) has described a method which employs vacuum sublimation in a hard glass tube for such highly volatile elements as Sb, As, Sn, Pb, Cd, Ag, and Ge. Observations have been made on *sphalerite* and *chalcopyrite* at pressures of about 10^{-4} – 10^{-5} mm Hg and temperatures up to 880°C. In the sublimate there is usually an enrichment of the very volatile elements. At this point, sensitivity of detection may often be increased by a spectrochemical analysis of the sublimate rather than the mineral itself. For purposes of quantitative analysis, completeness of sublimation must be ensured. The method of sublimation has potentialities of wide application to many sulfide ores.

Arsenic is probably the most ideal internal standard for antimony, and vice versa.

The spectrochemical limit of detection for bismuth is usually similar to that of antimony (0.001%) if Bi 3067, its most sensitive line, is used and this line is invariably employed. Bi 3067.716 is situated fairly close to Fe 3067.244, a relatively intense iron line which in iron-rich minerals causes considerable halation at λ 3067 A. Unless a small spectrograph is used, such halation does not cause actual interference, and Fe 3067 may be used to aid in quick identification of Bi 3067.

The bismuth concentration in many sulfide minerals is frequently below its detection limit. Sempels (1948) has employed a combination of fire assay and spectrochemical analysis on such minerals, and was able to detect as little as 0.0001% Bi. A lead button which contains all the bismuth is obtained, and this button is analyzed spectrochemically.

For the analysis of zinc, lines at three widely different wavelengths have been used. Zn 2138 (the most sensitive line), the two doublets at λλ 3302 and 3345, and the triplet 4680, 4722, and 4810. Unless plates sensitized to the ultraviolet are used (see below), Zn 3345 is usually employed and is regarded as the most sensitive line. Mitchell (1948) used this line for the analysis of zinc in a concentrate referred to in Chapter 11 and attempted to use iron as the internal standard. Unless the arc burn was very smooth, erratic results were obtained. These were attributed to the large difference in volatilities between iron and zinc. The use of cadmium as an internal standard was found satisfactory. When analyzing for zinc in *magnetite*, the temptation to use iron as an internal standard is sure to arise, but in view of the above observation this is not advisable for precise work.

Using Zn 3345, a detection limit of about 0.01% can be attained.

Zn 2138 has been used by O'Connor (1941) for the determination of zinc in fertilizers. Because of the high volatility of zinc, sensitivity could be enhanced by using relatively deep electrodes. A detection limit of 0.0002% is reported. This detection limit is far better than is usually attainable,

and should enable the analyst to determine zinc in many rocks, minerals, and soils where it is otherwise undetectable. Because the wavelength of Zn 2138 is below the sensitive range for normal photographic emulsions, ultraviolet sensitive types must be used. O'Connor, who mentions the possibility of interference from Fe 2138.589 and Cu 2138.507, found that in practice neither of these two lines was in evidence at 3% Fe and 1% Cu.

For the analysis of zinc in biological ash, Rogers (1935) also used Zn 2138 because of its high sensitivity.

The analysis of zinc in ores is described by Marks and Jones (1948), who used the procedure outlined in Chapter 11 (method of Marks and co-workers). A similar general method has been used by Schnopper and Adler (1949). In place of the usual $CaCO_3$ buffer employed by Marks and co-workers, these authors used Li_2CO_3 and added a 2:1 Li_2CO_3 and graphite mixture to each specimen. As a binder, a drop of saturated alcoholic sugar solution was added to each charge and was allowed to dry before arcing. Relatively short exposures of 20 seconds were used, because zinc was quickly volatilized by using anode excitation at 14 amp. A very satisfactory accuracy was attainable, and the authors claim a standard deviation of ± 6–7% over the wide concentration range of 0.05–6% Zn.

With the exception of Zn 2138, the low energy levels of all zinc lines usually employed for analysis are considerably above the ground state (4.0 volts). As a result, these lines do not readily self-absorb and for this reason may frequently be used over large concentration ranges. Their excitation potentials (again with the exception of Zn 2138) are also higher than those of most lines, and a cool alkali metal-rich arc is not conducive to their intense emission.

The well-known reagent dithizone has frequently been employed to concentrate elements prior to their analysis. Rohner (1938) describes the use of this reagent for the analysis of mercury and other elements in *pyrite*. A spark was used, but the dithizone procedure could probably be modified and employed in conjunction with the d.c. arc. Mitchell (1948, Chapter 11) points out that the concentration of elements effected by the use of dithizone as a reagent is particularly well suited to the high voltage a.c. arc because the electrode is treated with a few drops of solution. Mitchell gives many references to the use of dithizone for concentrating elements prior to spectrochemical analysis.

Additional references: Evrard (1945) for Cd; Bray (1942) for Zn; Rost (1939) for Zn; Szelenyi and Vogl (1941) for Sb; Abramov and Rusanov (1938) for Cd.

CHAPTER 21

Pb; Cu; Sn; Ge

21–1. Lead. Lead may frequently be detected in many common rocks, several minerals, and many soils. Often, however, its concentration borders on its limit of detection (usually about 0.001% or less), in which case detectability may depend on the spectrochemical procedure employed. Lead shows dual geochemical characteristics and, in addition, its presence in some minerals is largely due to radioactivity. Pb^{++} (radius 1.32 A) is a large cation capable of substituting for K^{+} (1.33 A) and to a lesser extent for Ca^{++} (1.08 A) in their respective minerals. Potash feldspar is a typical host mineral for traces of lead. In its other more familiar geochemical role, lead is commonly found in detectable amounts in a wide variety of sulfide minerals.

Because lead is a decay product of uranium and thorium, it is detectable in all their minerals and often also in *zircon*, *titanite* (*sphene*), and *apatite* which are accessory minerals in common rocks. Here a significant proportion of the lead is probably radiogenic. See the investigations of Larsen, Keevil, and Harrison (1949). It follows of course that the concentration of lead in these minerals is more likely to be within detectable range if the mineral is geologically old (pre-Cambrian).

The most sensitive line of lead is Pb 4057 but this line has not been in very common use so far because of interference from the CN band with head at 4216 A. However, van Tongeren (1938), who was restricted to the use of lines of relatively long wavelength, employed Pb 4057 for the analysis of lead in rocks. He used cathode layer excitation and found that in the presence of Na_2CO_3, CN emission was weakened considerably (Section 10–2). However, some CN emission was evident, and use was made of the difference in longitudinal intensity distribution of Pb 4057 and rotational lines of CN to distinguish between them in the arc. Because of the marked intensity increase of Pb 4057 near the cathode, this line is easily distinguishable from the CN rotational lines, which do not exhibit an enrichment effect. If anode excitation is used, CN emission can be removed almost entirely during the early period of arcing. Because lead is volatile, Pb 4057 can be recorded on a CN-free background, provided the instructions given in Section 10–2 are followed. It is then possible to detect and estimate lead in concentrations well below 0.001% (detection limit about 0.0002%). This enables the analyst to detect and determine lead in many basic rock types (diabase and gabbro, for example) where it

is otherwise not detectable. In such basic rock types the presence of Mn 4057.95 has been observed. Because the wavelength of this line is only 0.13 A greater than Pb 4057.820, a spectrograph of large dispersion is required to resolve the two lines. Mn 4057 is usually absent from acid rock types.

As lead is volatile, its accurate analysis requires the use of a volatile internal standard. In the Cabot Spectrographic Laboratory, indium has been used as an internal standard. The reproducibility is satisfactory. For analyses of lead in diabase and granite, reproducibility data are given in Chapter 11. Bismuth has also been used as an internal standard for lead. Pb 2833: Bi 3067 constitute the analysis pair. Several workers who have determined lead in biological ash have used bismuth as the internal standard. Pb 2833 is a commonly used lead line.

For the analysis of lead in ores, the method of Marks and co-workers (Chapter 11) was employed by Marks and Hall (1946).

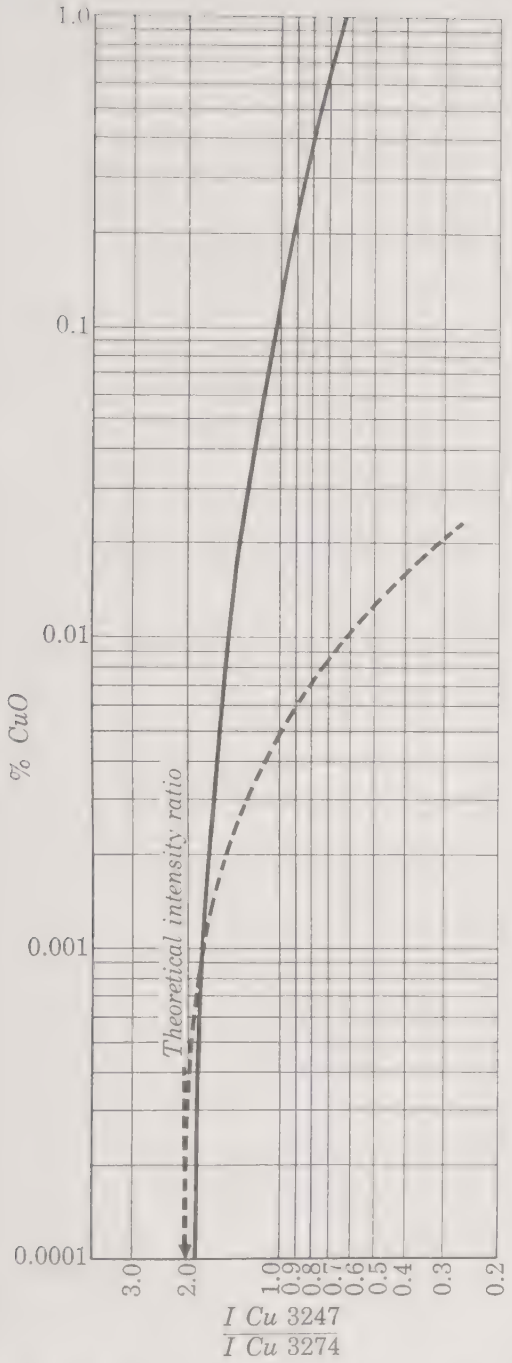
One example of the use of a pre-enrichment procedure is that of Fieldes (1942) who precipitated lead as the sulphate. After making the sulphate into pellets with ammonium sulphate, the pellets were arced. Mitchell (1948, Chapter 11) lists many publications which describe methods for concentrating lead in a variety of materials prior to their spectrochemical analysis.

Additional references: Sahama (1945 a and b), Nockolds and Mitchell (1948).

21–2. Copper. The spectrochemical sensitivity of copper is very high (detection limit 0.0001% and sometimes less), and because this element is widespread it may be detected in a variety of minerals, rocks, and soils. Cu^{++} is an ion of medium size which can substitute for Mg^{++} and Fe^{++}. As a result, minerals which offer octahedral structure sites often contain significant traces of copper. The ferromagnesian minerals are typical examples. Copper is also detectable in a wide variety of sulfide minerals; in many of these it is very considerably enriched.

There are only two very sensitive lines of copper, Cu 3247 and 3274. Both are components of the same multiplet. Cu 3247 is the more sensitive, and the ratio $\frac{I \text{ Cu } 3247}{I \text{ Cu } 3274}$ approaches 2.0 (see below).

Trouble is quite frequently caused by the presence of copper in the graphite or carbon when very small amounts are analyzed. The degree of this interference is probably lessened by using low amperage anode excitation. Using the carbon manufactured by National Carbon Company an the method described in Chapter 11 (indium as internal standard), it has been possible to determine copper with apparent success at *very* low con-



centrations (near detection limit) with reasonable accuracy. A good example is granite (Chapter 11), where the concentration is often as low as ~0.001%. Electrode copper is inhomogeneously distributed and if its concentration were significant at these low concentrations, reproducibility would be far worse. Furthermore, a working curve does not indicate the presence of significant traces of copper even at very low concentrations.

The slope of the copper working curve is less than 45° and there is some evidence that this is due to self-absorption, which particularly in Cu 3247 seems to begin at extremely low concentrations but does not appear to increase very sharply under the working conditions employed. (Ag 3280 shows this same tendency.) Fig. 21–1 shows a plot of log $\frac{I \text{ Cu } 3247}{I \text{ Cu } 3274}$ vs log% CuO, using the same working conditions as for indium as internal standard (Chapter 11). Even at extremely low concentrations of copper Cu 3247 begins to absorb, and the ratio $\frac{I \text{ Cu } 3247}{I \text{ Cu } 3274}$ decreases with increase in concentration. Because Cu 3274 is a little less intense than Cu 3247, it will

Fig. 21–1. In this plot of I Cu 3247/I Cu 3274 vs % CuO, the ratio is seen to decrease below 2.0 at very low copper concentrations, indicating self-absorption first by Cu 3247. The rate of decrease of ratio with increase of concentration is, however, extremely slow; compare the form of the curve for Cu 3247/Cu 3274 with that of K 4044/K 4047 (Fig. 7–10) which has been shown here (broken curve) for comparison. The position of this comparison curve with respect to the ordinate is not correct (Fig. 7–10) but is positioned for ease of comparison.

begin to self-absorb at slightly higher copper concentrations. However, this rate of change is very slight. Compare with Fig. 7–10 (log $\frac{I \text{ K } 4044}{I \text{ K } 4047}$ vs log% K_2O).

Carobbi and Pieruccini (1943) have employed iron as a variable internal standard for the analysis of copper in sedimentary rocks. Cathode layer excitation was employed, and specimens were loaded into a relatively deep cathode (12 mm) and arced for five minutes. The authors describe a procedure for making a blank copper determination (base + electrodes) which utilizes a CN band component (CN 3160) as a reference intensity standard. In a later paper, Pieruccini (1946 b) states that copper determinations can usually be made within ±7% of the correct amount, using iron as the variable internal standard.

Silver is probably the ideal internal standard for the analysis of copper. Unfortunately, however, disturbing amounts of silver are likely to be present in sulfide minerals. Interference is unlikely in many silicate minerals, rocks, and soils, but should be checked in basic rocks. Farmer (1946) has demonstrated the efficacy of silver as an internal standard for copper.

Additional references: Nockolds and Mitchell (1948), Bray (1942) re Cu in electrodes.

21-3 Tin. In many granitelike rocks the magnitude of the tin concentration is about 0.01%; this amount is easily detectable. In basic rock types, about $^1/_{10}$ of the tin content of granite is likely to be present. This concentration of 0.001% is the approximate spectrochemical detection limit for tin, and consequently tin is not easily detected in basic rocks. Usually it is reported as "not detectable" in such specimens. In the common silicate minerals, tin tends to concentrate in *micas*, notably those from pegmatites. It is sometimes detectable in soils, and is a typical constituent of many sulfide minerals.

Sn 3175 is probably the most sensitive tin line. Sn 2839 is of approximately equal sensitivity. These two lines have most commonly been used, although some interference may occasionally be present (see wavelength tables at end of this book). In particular Cr 2840.021 and Mn 2840.001 may interfere with Sn 2839.989. Should there be interference, several other relatively sensitive tin lines might be used.

Oftedal (1941) employed cathode layer excitation for the analysis of tin in *galena* and *sphalerite*. In both of these common minerals it was possible to use weak lines of the major constituents (lead and zinc, respectively) as internal standard lines. Because Pb, Zn, and Sn are all volatile and have conveniently placed lines of suitable excitation characteristics, such internal

standardization should be very satisfactory. Oftedal reports that most analyses could be made within ±5% of the correct amount. The analysis pairs used were Sn 3175:Pb 2873 and Sn 3175:Pb 3072. Using an entirely different method of introducing the specimen into the arc, Rusanov and Movchan (1941) reported a similar accuracy. The powdered sulfide minerals were introduced into the arc on paper strips. Bismuth served as an internal standard, and the analysis pair was Sn 3034:Bi 3024. A satisfactory accuracy is reported by Kuzmina (1937) for the analysis of tin in gold slime. This author employed a 4.5–5 amp arc between two slowly revolving copper discs 1 mm thick and 2 mm apart. Tin was determined over the concentration range 0.001–0.01%. The general method of Marks and co-workers (Chapter 11) has been applied to the analysis of tin in ores.

The general procedure described for thallium (Section 15–3) has been used by Ahrens and Liebenberg (1950) for the analysis of tin in mica. Sn 3262.328 was used. If a relatively small spectrograph is used, Ti 3261.605 is likely to cause interference because it is emitted with considerable intensity in many minerals, rocks, and soils. For the accurate analysis of tin in silicates (mica, granitelike rocks and some soils) use could probably be made of the method described in Chapter 11, which utilizes indium as an internal standard.

Additional references: Goldschmidt and Peters (1933 b), Ratsbaum (1938), Nedler (1936), Moritz and Schneiderhöhn (1936), Barsanov (1941), Szelenyi and Vogl (1941), Ottemann (1940).

21–4. Germanium. The spectrograph has been used very effectively to obtain information on the distribution of germanium in the earth's crust. A little more than two decades ago this element was considered very rare indeed, but as a result of many spectrochemical analyses (Papish, 1928, 1929, Goldschmidt and Peters, 1933 a) the ubiquity of this element in small amounts in many common silicate mineral and rock types has been demonstrated. Here we have another example of an element which, like gallium and scandium, is distributed very widely and with relative uniformity. Germanium is less common than gallium and is often found in concentrations which border on its detection limit. The reason for the widespread distribution of traces of germanium lies in its association with silicon. The radius of Ge^{++++} is 0.44 A, which enables this ion to substitute for Si^{++++} (radius 0.39 A). In the silicate minerals of relatively late crystallization (*topaz* and *lepidolite*, for example) there appears to be some enrichment of germanium. This follows because the radius of Ge^{++++} > radius Si^{++++}. Like several other elements (Ga, In, Tl, Zn, Ni, and others), germanium exhibits dual geochemical characteristics and it is also detectable in many sulfide minerals.

Either Ge 2651, the most sensitive germanium line, or Ge 3039, slightly less sensitive, is invariably employed.

Goldschmidt and Peters (1933 a) employed cathode layer excitation for their investigation on the geochemistry of germanium. Germanium is very volatile and these authors noted how sensitivity could be improved by increasing the cathode depth. Using a 7 mm cathode depth and Ge 2651, 0.001% or less germanium could be detected. A still greater sensitivity (detection limit ~0.0001%) was obtained by using a deeper and larger electrode and by recording only the relatively early period of arcing. Oftedal (1941) also claims a detection limit of about 0.0001%. Goldschmidt and Peters give details of various ways in which many of the different minerals were prepared prior to their analysis.

An enrichment procedure for the analysis of germanium in silicates has been employed by Rankama (1939). This method is based on the enrichment of GeO_2 in the silica residue after the usual Na_2CO_3 fusion and subsequent acid treatment in a standard analysis for silica. HNO_3 must, however, be substituted for HCl, otherwise there may be a loss of germanium chloride. Further enrichment of germanium in the silica residue may be effected by treatment with HF followed by H_2SO_4.

Germanium quite frequently enriches in coal and has been sought there spectrochemically by Goldschmidt and Peters (1933 a), among others. Coal is ashed before it is arced, but because of the ease with which germanium volatilizes there is a risk that some germanium will be lost. Even at temperatures of 500–600°C, some germanium might volatilize. Goldschmidt and Peters recommend that the coal specimen be treated with concentrated HNO_3 before ashing.

For the analysis of germanium in minerals, Rusanov (1940) has employed his usual method, namely, that of introducing the powdered mineral into the arc on paper strips. NaCl was used as a buffer and was loaded into cored carbon electrodes. The author states that by using bismuth as an internal standard, most germanium determinations can be made within ±5–8% of the correct amount. This is a reasonable accuracy and indicates that the use of the less conventional paper-strip procedure to introduce the specimen into the arc is quite satisfactory for some purposes. See also Section 21–3.

The use of an interrupted arc for the analysis of germanium in silicate minerals and rocks is described by Landergren (Wickman, 1943). Using Ge 2754, a detection limit of a little less than 0.0001% is reported. For the preparation of a base for standards, Landergren was able to use a natural silicate (*feldspar*) which was free from detectable amounts of germanium.

In ores, the method of Marks and co-workers (Chapter 11) has been used by Marks and Hall (1946).

Although *sphalerite* is one of the chief host minerals for germanium, the concentration in many specimens is lower than the spectrochemical detection limit (Oftedal, 1941 and Strock, 1945). For the analysis of germanium at these low concentrations ($\sim$0.0001%), the method of vacuum sublimation described by Veselovskii (1941) may be used (see Chapter 20). Thus no germanium ($<$0.0001%) was detectable in a specimen of *sphalerite*, whereas in its sublimate germanium was easily detected and was determined as 0.001%.

Additional references: Borovik and Kalinin (1939), Borovik (1941), Rusanov and Kostrikin (1936), Cambi and Maletesta (1936), Kuzmina (1938), Mitchell (1948, p. 123), Szelenyi and Vogl (1941), Abramov and Rusanov (1938).

CHAPTER 22

Ni AND Co; V; Cr

Ni, Co, V, and Cr are among those elements most frequently detected and determined in the spectrochemical analysis of minerals, rocks, and soils.

22–1. Nickel and cobalt. Nickel and cobalt have ions of medium size (radius Ni^{++} = 0.78 A and radius Co^{++} = 0.83 A). These elements tend to concentrate in detectable amounts in minerals which offer octahedral structure sites, notably the ferromagnesian minerals. In the more basic rock types nickel and cobalt are easily detectable, but in granitelike rocks nickel in particular may be present at a concentration below its detection limit. This limit is about 0.0002% for both elements. Nickel and cobalt exhibit dual geochemical properties. In addition to their distribution in many silicate minerals, they readily enter several of the sulfide minerals, where they may easily be detected spectrochemically.

Sensitive lines for both elements are conveniently placed within commonly used wavelength ranges. Ni 3414 and Co 3453 are the most sensitive and most commonly used lines. Like all other transitional elements, however, they have many sensitive lines, and the analyst will usually have a wide selection.

Nickel and cobalt are elements of medium volatility and are commonly associated with iron in iron-rich minerals and rocks. Consequently, iron has often been used as an internal standard. One of the earliest of such applications is described by Preuss (1935) who used iron as a variable internal standard for the analysis of nickel (and some other elements) in *tektites* (a type of natural glass). In these the iron content varied from 1.0–6.4% FeO. A similar general procedure has been employed quite extensively by Pieruccini (1946, a and b) for the analysis of many rock types, including *serpentines* relatively rich in nickel. As in the method described by Preuss, cathode layer excitation was employed. For the preparation of a synthetic base material of varying iron content, MgO, Al_2O_3, SiO_2, and Fe_2O_3 were used. The percentages of MgO and Al_2O_3 (10% and 15% respectively) were held constant, whereas SiO_2 was made to vary (73–45%) inversely with Fe_2O_3 (2–30%). In the unknowns the iron content ranged from 2–14% Fe_2O_3. Many analysis pairs were used: Ni 3414 and 3461 with Fe 3459, 3417, 3415, 3413, 3411, and 3401. By using each of a number of line pairs over a limited Ni/Fe concentration range only, approximate equality of intensity of analysis line and internal standard line can be

maintained. This is helpful for accurate intensity ratio measurements, particularly in the presence of heavy background. The above synthetic standards could not be used for rocks rich in lime (> 40%) because the analysis line pairs were not sufficiently stable to compositional changes of that type.

The general method using palladium as an internal standard (Chapter 11) may be employed for the analysis of nickel and cobalt in silicates.

The method developed at the Macaulay Institute, Aberdeen, for using iron as a variable internal standard (Scott, 1946; Mitchell, 1948) has been particularly successful for the analysis of cobalt. Using cathode layer excitation and the line pair Co 3453: Fe 3451 (respective excitation potentials, 4.0 and 5.8 volts), a standard deviation of ±4.0% is obtainable. Not only is the intensity ratio of this analysis pair highly reproducible in one matrix, but it is relatively stable to large compositional changes. The stability of this analysis pair compared with the analysis pairs of many other elements (with iron as internal standard for all) may be seen by an inspection of Table 8–1. The excitation potential difference of 1.8 volts for Co 3453 and Fe 3451 does not appear to be large enough to lower reproducibility. Table 8–1 shows the intensity ratio of the analysis pair for nickel (Ni 3414: Fe 3413) to be reasonably stable compared with most analysis pairs except in the SiO_2 base, where the intensity of Ni 3414 has a marked maximum.

Rost (1939) investigated the nickel: cobalt association in many sulfide minerals. He found that these arced poorly. Consequently, each mineral powder was first heated and oxidized slowly, and then mixed with two parts of quartz powder and arced, to produce a melt which arcs reasonably well. In some specimens of *pyrite* a relatively high accuracy was required for cobalt. For this purpose iron was used as the internal standard. Hegemann (1943), who determined nickel and cobalt in *pyrite*, was able to find some pure *pyrite* free from detectable concentrations of nickel and cobalt. This was used as base material to which varying amounts of Co_3O_4 and NiO were added.

Additional references: Davidson and Mitchell (1940 a), Sahama (1945 a and b), Prokofev (1937), Wager and Mitchell (1943), Nockolds and Mitchell (1948), Bray (1942), Fitz and Murray (1945), Lundegardh (1946), Strock (1945), Nedler (1936), Stoiber (1940), Oftedal (1941), Evrard (1945), Preuss (1937), and Matveev (1939).

22–2. Vanadium. Like the ions of the other three elements discussed in this chapter, V^{+++} is of medium size (radius 0.66 A). As a consequence, it readily enters minerals octahedrally; the ferromagnesian minerals are typical host minerals. The more basic rock types usually have more

vanadium than granitelike types. Unlike nickel and cobalt, vanadium is not a normal minor constituent of the sulfide minerals.

The vanadium lines most commonly used are V 3185 (or V 3184) and V 4379. These are the most sensitive components of two quite widely separated multiplet groups. By using these lines, the analyst is usually able to detect vanadium down to about 0.001–0.0005%. Vanadium also has some sensitive ion lines which are occasionally used (see below).

In common with the other elements discussed in this chapter, vanadium is of medium volatility, and it is not surprising that because of its relatively close association with iron this element has quite frequently been used as an internal standard. Preuss (1937) describes the use of iron as a variable internal standard for the analysis of vanadium in waste ore. When cathode layer excitation and the line pair V 3184: Fe 3100 were employed, most analyses could be made within ±7% of the correct vanadium content. Iron has also been used as a variable internal standard for the analysis of vanadium by Scott (1946). See also Mitchell (1948).

Preuss (1938) employed the method described in his earlier paper (1937) for the analysis of vanadium in mineral specimens of *graphite*. He analyzed the untreated mineral and its ash and found that the intensity ratio of the analysis pair remained constant. Vanadium concentrations of 0.01–0.05% were found. He undertook this investigation on *graphite* because previous spectrochemical analyses of this material by Maucher (1936), gave a surprisingly high vanadium content (0.1–0.5%), and a check was needed. Other spectrochemical analyses by Bader (1937), who employed an interrupted arc and copper electrodes, corroborated the analyses of Preuss. Bader used the ion line pair V 3118: Fe 3119.

Maucher had used the sensitive vanadium ion lines V 3102, 3111, and 3118. He arced the untreated *graphite* and compared the analysis line intensities with those emitted from standards of different composition. Here is an example of an unusually large error (5–10 ×) caused by comparing intensities in unlike matrices, and is very probably due to the use of ion lines. When the *graphite* specimen was arced, the arc was essentially a carbon arc in air and intensely hot. The degree of ionization was therefore high, and the vanadium ion lines would be much enhanced. Since the comparison standard contained elements whose ionization potentials were considerably lower than that of carbon a very marked weakening of the vanadium ion lines in the resultant cooler arc is not surprising when Saha's relationship (Section 3–3) is taken into account.

The general method of using palladium as an internal standard (Chapter 11) applies to vanadium.

Magnetite (and iron ore in general) is one of the common minerals in which vanadium is often sought. Because of the popular use of iron as

an internal standard for vanadium, it is a logical choice for the analysis of magnetite. Kvalheim (1941) successfully used the analysis pair V 3185: Fe 3205 for the analysis of vanadium in iron ore. In the presence of silicate gangue minerals, however, the intensity ratio appeared to be disturbed. Kvalheim consequently investigated the effect of compositional variation on the intensity ratio of the analysis pair and found it very sensitive to matrix variations. This is shown in Fig. 22–1, which is adapted from Kvalheim (1941). $CaCO_3$ is seen to enhance the intensity of V 3185 more than any other added compound. Because of the sensitivity of the V: Fe analysis pair to compositional changes, the use of chromium as an internal standard was attempted. The analysis pair V 3056: Cr 3034 was used and proved very stable. The excitation potential of V 3056 is 4.06 volts and that of Cr 3034 is 5.07 volts. This difference of 1.01 volts is apparently not significant for the range which was investigated.

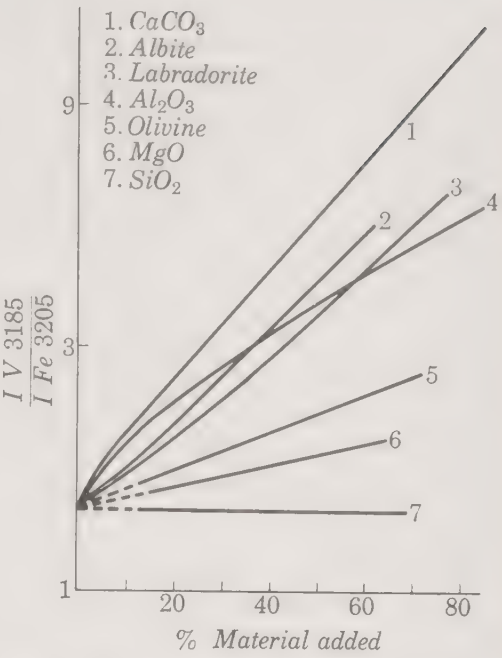


Fig. 22–1. These curves show that V 3185 emits a maximum intensity with respect to Fe 3205 in a matrix of $CaCO_3$.

Observations by Scott (1945) on the effect of $CaCO_3$ on the intensity of vanadium lines have corroborated those of Kvalheim. For V 3185, a very marked intensity increase was found (see Table 8–1). On the other hand, the intensity of V 4379 was enhanced to a much smaller degree. Because $CaCO_3$ enhances the intensity of V 3185 so very markedly, its addition to samples for the purpose of attaining optimum sensitivity is indicated.

A trace of vanadium is a troublesome contaminant even of high grade electrode graphite or carbon.

Additional references: Van Tongeren (1938), Wager and Mitchell (1943), Nockolds and Mitchell (1948), Borovik (1943 c), Preuss (1935), Sahama (1945 a and b).

22–3. Chromium. The stable chromium ion Cr^{+++} is of medium size (radius 0.64 A), and the general comments made about the distribution of Ni, Co, and V in the common silicate minerals and rocks pertain also

to chromium. The concentration of this element usually changes very sharply in different rock types. In basic types, chromium is markedly enriched, whereas in granite rocks its concentration may be so low that despite its very high sensitivity (detection limit 0.0001% or less), chromium may not even be detectable. Unlike nickel and cobalt, chromium is not readily accommodated in sulfide minerals, nor is it usually sought there.

Cr 4254, a member of the sensitive multiplet 4254, 4274, and 4289, is the most sensitive chromium line. It is commonly employed for detecting and determining low concentrations of chromium.

Chromium is a moderately volatile element, and several of the methods referred to in Section 22–1 and Section 22–2 apply here as well. See, for example, Pieruccini (1946 a and b) and Scott (1946). Pieruccini used Cr 4254 and 4289 with Fe 4294, 4282, 4247, 4235, and 4233, and with these lines, he was successful in covering a relatively large concentration range (from as little as 0.0003% Cr_2O_3 in granite to as much as 1.4% Cr_2O_3 in *serpentine*).

Additional references: Van Tongeren (1938), Goldschmidt and Peters (1933 b), Sahama (1945 a and b), Wager and Mitchell (1943), Nockolds and Mitchell (1948), Davidson and Mitchell (1940 a and b), Lundegardh (1946), Preuss (1935), Papish and O'Leary (1931).

CHAPTER 23

COMMON ELEMENTS USUALLY PRESENT AS MAJOR CONSTITUENTS

(Si, Al, Ca, Mg, Fe, Mn, Ti, K, AND Na)

23–1. Introduction. Spectrochemical analysis is usually considered a useful method for detecting and estimating trace constituents in various materials. In each of the foregoing chapters of Part II the discussion on each element has usually been from the point of view of its analysis as a minor element. However, there has been a recent trend to widen the scope of spectrochemical analysis. Attempts have been made to develop reasonably accurate quantitative methods for the analysis of the common elements which are the major constituents of many minerals and all rocks and soils. In endeavoring to develop such methods, the analyst has always been aware that the accuracy of the best spectrochemical method will rarely compete with that of standard chemical methods (potassium is one possible exception; Section 23–3) and consequently the object has not been to supplant chemical methods where highest accuracy is required. Chemical analysis of a mineral, rock, or soil is, however, very time-consuming and costly, and is ill-adapted to the rapid analysis of many specimens. Provided that highest accuracy is not required, spectrochemical methods could fulfill the need for a method that is rapid and yet reasonably accurate. By "reasonably accurate" is meant a standard deviation of ± 4–5% or less.

A few applications of quantitative spectrochemical methods in the analysis of major constituents are listed below.

(1) A rapid spectrochemical survey may be made of a suite of rocks, and the resultant analytical data should aid the petrologist in selecting specimens for a more accurate chemical analysis. The accuracy of spectrochemical methods appears adequate for a study of the behavior of the common elements at igneous rock contacts. Observations of this type have been made in the Department of Geology, M. I. T. (Dennen, 1949).

(2) When investigating the distribution of minor elements in minerals and rocks, a study of minor:major element associations becomes highly desirable (Ge:Si, Ga:Al are examples). Usually many specimens are investigated and, because very accurate determinations of the major elements are not necessary, the use of spectrochemical methods applies here.

(3) A spectrochemical method is well adapted to the analysis of the

major components of a mineral when only a very small quantity (a few mg at most) of specimen is available (Section 23–4).

(4) Spectrochemical analysis has been applied to some extent to the wide variety of materials used in the ceramic industry (Jaycox, 1947).

(5) Some elements are particularly awkward to analyze chemically when in the presence of other elements which have similar chemical properties. The analysis of niobium and tantalum in concentrates from their ores (Section 19–3) and the rare earth elements in rare earth mixtures (Chapter 16) are examples of the use of spectrochemical methods for elements difficult to analyze by chemical means.

(6) The analysis of slag (see, for example, Korzh, 1945 and Rozsa, 1947) is another application of d.c. arc methods for major constituents.

(7) For analysis of the major components of soils spectrochemical methods rapidly establish soil composition (inorganic constituents) with a reasonable degree of accuracy.

23–2. A method developed by Kvalheim (1947) especially for minerals and rocks. Two procedures are described; one for the analysis of Si, and the other for Al, Ca, Mg, Fe, Mn, and, in somewhat modified form, K and Na. For the analysis of silicon, cathode excitation was employed, and beryllium, added as BeO or $BeCO_3$, served as the internal standard. Usable analysis pairs are Be 2494 and weaker members of the silicon multiplet group at 2530 A. Ordinarily beryllium is much less volatile than silicon, but in this method NaCl and powdered carbon are added (1 part sample + 1 part $BeCO_3$ + 3 parts NaCl) and this difference is minimized. Fig. 6–2 (No. 2) shows volatilization curves for silicon and beryllium under these conditions of working. These curves are based on measurements made by Mrs. L. G. Gorfinkle in the Cabot Spectrographic Laboratory.

Although the trends in the two curves are reasonably close, attempts were made to smooth out the differences in the hope of improving the reproducibility, which was determined as about ±6.5%. NaCl was omitted and each specimen was heavily diluted with carbon powder (14 parts carbon powder and 1 part specimen). Fig. 6–2 (No. 3) shows volatilization curves in the presence of 14 parts carbon. The curves are very similar; this is shown more clearly in Fig. 23–1, a plot of $\frac{I \text{ Si } 2528}{I \text{ Be } 2494}$ vs time. This curve remains very nearly horizontal throughout the whole period of arcing. As a result, an improvement in reproducibility was expected and was found. Some typical reproducibility data on diorite are given in Table 23–1; the standard deviation is calculated as ±3.5%.

For the analysis of Al, Ca, Mg, Fe, Mn, Na, and K, strontium was used as the internal standard (see Section 7–6 for comments on the possibility

of interference from strontium already present in the rock). Anode excitation, using a small cathode layer type of anode, was employed for Al, Ca, Mg, Fe, and Mn. Cathode excitation was used for K, while either anode or cathode excitation could be used for Na. Dennen (1949) has utilized this method (except for potassium) for investigating the behavior of the common elements at igneous rock contacts; he shows several volatilization curves and longitudinal intensity plots. A statistical examination of reproducibilities showed that standard deviations are usually about ±4–6%.

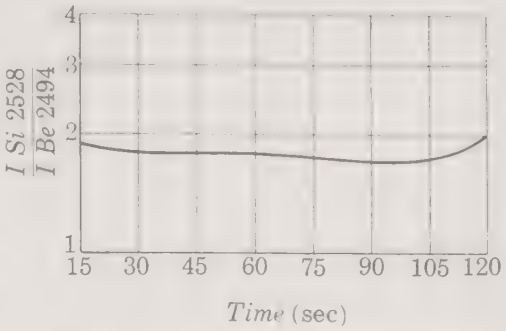


Fig. 23–1. This plot shows that in the presence of high dilution with carbon powder, the ratio *I* Si 2528/*I* Be 2494 remains nearly uniform during the whole period of arcing.

Little is known about the effects of compositional changes on the intensity ratios in these methods. The plotted points in Kvalheim's graphs refer to a relatively wide compositional change, and their locations indicate that such effects are not very great. A thorough investigation of the effect of compositional changes seems desirable here, however. Strock (1948 a) has

Table 23-1

	% SiO_2	% dev. from mean
	61.5	-1.6
	63.0	+0.8
	59.7	-4.5
	66.5	+6.4
	63.8	+2.1
	61.0	-2.4
	61.0	-2.4
	62.0	-0.8
	63.8	+2.1
	62.5	0.0
	64.7	+3.5
	66.9	+7.0
	63.8	+2.1
	63.4	+1.8
	60.2	-3.7
	58.7	-6.1
	63.0	+0.8
	62.5	0.0
Mean	62.5	Standard deviation ±3.5%

used germanium as a flux for analyses of major constituents. As the flux destroys mineral structures by readily forming a molten globule the influence of compositional variation on line intensity is reduced (see Section 8–7).

The possible influence of compositional variation on the intensity of major constituent elements does not as a rule pose so acute a problem as when trace constituents are sought. It is usually possible to obtain accurately analyzed minerals, rocks, and soils, and the need for synthetic standards does not arise. Furthermore, since analyzed specimens covering a relatively wide spread of types are obtainable, it is easy to prepare separate working curves (if necessary) for each specimen type to be analyzed.

23–3. Potassium in feldspar. The chemical analysis of potassium in the presence of high concentrations of sodium is often difficult. In the Cabot Spectrographic Laboratory an investigation has been undertaken (mainly by F. C. Canney) to develop a very accurate spectrochemical method for the analysis of potassium in *feldspar*. Thus far, most observations have been made on *albite*. Rubidium has been used as the internal standard with excellent results. Rubidium and potassium volatilize almost identically, and the excitation potentials of K 4044 and 4047 and Rb 4202 are very similar. The longitudinal intensity distribution of K 4044–7 is almost identical with that of Rb 4202. Anode excitation (7 amp) was employed, and in the presence of much alkali metal vapor from feldspar, CN emission caused no interference. Standard feldspars (National Bureau of Standards), one *albite* and one *microcline*, were mixed and used as standards.

Table 23-2

% K_2O	% deviation from correct value
0.98	-2.0
0.98	-2.0
1.02	+2.0
0.97	-3.0
0.95	-5.0
1.01	+1.0
1.04	+4.0
1.01	+1.0
1.01	+1.0
0.98	-2.0
1.06	+6.0

True concentration 1.00 Standard deviation ±3.1%

Table 23–2 gives a good indication of the high reproducibility of the method. The approximate standard deviation is ±3.1%.

Some observations have also been made on the use of lithium as an internal standard for the analysis of K, and also Na, Rb, and Cs, in rocks. This investigation is not complete, but results thus far are very satisfactory.

Helz (1945) used silver as an internal standard for the analysis of potassium (and also sodium) in cement. The standard deviation was ±8.1% for potassium and ±5.7% for sodium. For the analysis of potassium in rock salt, Haycock and Russell (1948) used copper as an internal standard. Copper has also been used as an internal standard for the analysis of potassium in biological ash.

There is little doubt that rubidium is an ideal internal standard for potassium, but its use is restricted. Because of the close geochemical association of these two elements, rubidium may be present in concentrations sufficient to cause interference. In *albite*, however, such interference appears to be negligible. These minerals rarely contain more than about 0.005% Rb_2O, whereas the amount of Rb_2O used as internal standard is 1.0%. To safeguard against possible interference, a blank analysis may be made.

23–4. Method of Jaycox (1947). Although this method was developed primarily for the analysis of several major constituent elements in ceramic materials, it may also be applied to minerals, rocks, and soils.

To counter possible self-absorption at high concentrations and to reduce the intensities of the major constituent lines to measurable levels, extreme dilution of each sample is made by the addition of many parts of CuO and carbon powder. Copper is used as the internal standard and, because of its high concentration, serves as a buffer. Different ratios of sample: CuO:C have been used. These ratios depend upon the concentrations of the elements sought. Common ratios are 1:9:20, 1:19:40, and 1:39:80.

Extreme dilution with CuO and carbon powder is an aid in obtaining high accuracy because it reduces selective volatilization considerably. As a result, comparatively volatile copper has been employed successfully as an internal standard for the analysis of relatively involatile aluminum and calcium. Anode excitation was employed, and the agreement between chemical and spectrochemical data is generally very good. Most determinations accord within ±4%. Table 23–3 shows some comparative analyses of a specimen of *talc*.

Korzh (1945), who also used CuO as an internal standard, describes methods for the analysis of Ca, Al, Si, Fe, Mg, and Mn in slag. However, CuO was not added in excess, nor was it used as a buffer. A method similar in some ways to that of Jaycox (1947) is one described by Oshry, Ballard,

Table 23-3

	Spectrochemical (%)	Chemical (%)
Al_2O_3	1.07	1.15
CaO	0.42	0.43
Fe_2O_3	1.37	1.39
MgO	31.6	31.2
SiO_2	57.2	58.8

and Schrenk (1942) for the analysis of Si, Fe, and Al in mineral powders. NiO is used as the internal standard-buffer diluent in place of CuO. Instead of the usual low voltage d.c. arc, a high voltage (2200-volt) source was used. Smith and Hoagbin (1946) determined sodium and silicon in alumina and used lithium and manganese as the respective internal standards. Employing the line pairs Na 3302: Li 3232 and Si 2438: Mn 2430, good reproducibility was reported, which when expressed as standard deviation was about $\pm 5\%$. 10-amp anode excitation was used and each sample was diluted with 2 parts graphite + internal standard mixture.

23–5. Method of Fitz and Murray (1945), developed and used particularly for very small samples. This method was developed particularly for the analysis of specimens which were available only in very small quantities (1.0 mg or less). It is generally applicable to all types of powders. Barium (as nitrate) is used as an internal standard-buffer and use is made of $(NH_4)_2SO_4$ to help volatilize the specimen quickly. Ratio of specimen: $Ba(NO_3)_2$: $(NH_4)_2SO_4$ = 1:10:10. Using 6–7 amp anode excitation, determinations can usually be made within $\pm 10\%$.

A method capable of handling very small samples satisfactorily would find application to the analysis of the major and some minor components of minerals which are not obtainable in sufficient quantity for chemical analysis. An example is furnished by small inclusions in sulfide minerals. Rennhackkamp (1949) describes the application of the method of Fitz and Murray to the analysis of minerals of this sort. The specimens had first to be isolated under the microscope by means of a microdrill sampling technique (Section 5–1). As little as 0.017 mg of specimen was analyzed. Analyses were made of gold, silver, and copper ores.

23–6. Some comments on the detection of the common elements and their quantitative analysis as trace constituents.

Aluminum. Aluminum has two widely spaced sensitive doublets, the most sensitive components of which are Al 3961 and 3092. The former is slightly more sensitive. Using these lines, the detection limit is about 0.001% or less. Aluminum is fairly involatile, and when common silicates are arced it tends to form a residual alumina bead which is very difficult to arc. In Section 5–2 methods are described for preventing the formation of a residual alumina globule.

Calcium. Calcium shows a high sensitivity, and its detection limit is about 0.00005%. Either the ion line (Ca 3933) or the atom line (Ca 4226) may be regarded as the most sensitive. Ca 4226 is more sensitive when the arc is relatively cool (when alkali metal-rich minerals are analyzed), whereas Ca 3933 is more sensitive in a relatively hot arc (when, for example, calcium is sought in carbon or graphite). See Section 5–7 and also compare the observations on titanium.

Calcium has been sought as a minor constituent in very ancient (2000×10^6 years) potassium-rich minerals (micas) where, it was thought, a relative enrichment of radiogenic calcium (from β-decay of K^{40}) might be found (Ahrens and Evans, 1948). The range 0.001–0.02% calcium was investigated without internal standardization, but more recently Ahrens (unpublished data) has tried barium as an internal standard. Several atom and ion line pairs have been used, and barium has been found satisfactory,

Table 23-4

Matrix	Ionization potential	I Ti II 3387 / I Ti I 3385
KCl	4.3	0.50
NaCl	5.1	0.50
$BaCl_2$	5.2	0.58
Al_2O_3	6.0	0.78
$CaCO_3$	6.1	0.59
MgO	7.6	0.74
SiO_2	8.1	1.40
BeO	9.3	1.55
C	11.2	1.95

even when the arc burn was erratic, provided the anion was the same for both elements.

Titanium. Titanium emits many sensitive lines from both atom and ion; none are outstandingly sensitive. Some of the most sensitive titanium lines are Ti 4981, 3653, 3383, and 3349.

The comments about the relative sensitivities of calcium atom and ion lines (Section 5–7) apply here also. Preuss (1938) has given a good indication of the relative intensity changes of titanium atom and ion lines in different matrices. He measured the intensity ratio of $\frac{\text{Ti II } 3387}{\text{Ti I } 3385}$ in different matrices and employed cathode layer excitation. His results are generally instructive and are shown in Table 23–4. The intensity ratio varies by a factor of almost four. Ion line emission (Ti 3387) is most intense in the presence of elements of high ionization potential, whereas emission from the atom (Ti 3385) is most intense in a cool arc (presence of elements of low ionization potential). Fig. 23–2 is a graphic portrayal of the relationship between log ionization potential and log $\frac{I \text{ Ti } 3387}{I \text{ Ti } 3385}$.

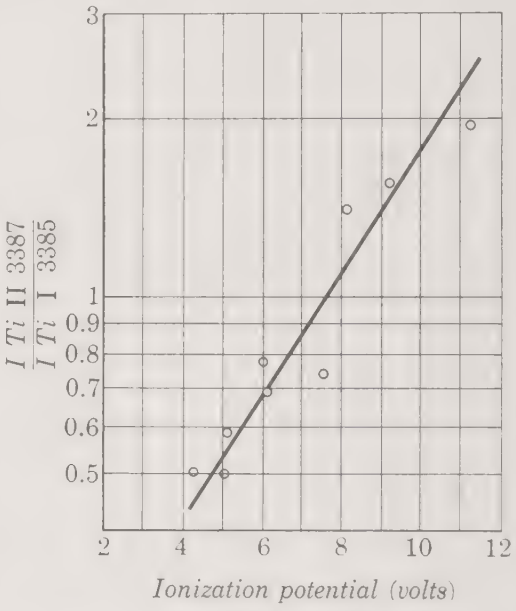


Fig. 23–2. The ratio of a titanium atom-ion line pair is seen to vary sharply with the ionization potential (and hence temperature) of the arc gas. This relationship is general for all atom-ion line pairs.

Titanium volatilization in the arc is characteristic and prolonged. Titanium is most accurately classified as an involatile element, but its lines invariably show quite early with some intensity, even in the absence of carbon or ammonium salt admixture. Peak intensity of emission is usually towards the end of the arcing period, and titanium lines may be among the last to fade out.

Manganese. For the detection of manganese, its most sensitive line, Mn 4030 (a component of the closely spaced triplet, Mn 4030, 4033, and 4034), is usually employed. Its detection limit is about 0.0005–0.0001%. Mn 4030 is located in a weak part of the band with head at 4216 A. If the arc burn has been particularly poor, CN interference may develop, and

other sensitive manganese lines situated at considerably shorter wavelengths may then be employed. Two of these are Mn 2576 and 2794. Mn 2576 is an ion line.

Manganese may be regarded as of medium volatility, although it is usually somewhat more volatile than iron.

Iron. For the detection of this very common transitional element, a wide selection of sensitive lines is available to the analyst. Fe 3581 is the most sensitive iron line, but is rarely used because it is located within an intense part of CN 3590. Fe 3720 and Fe 3020 are other very sensitive iron lines. Using these lines, the detection limit is about 0.0005–0.0001%.

Iron is an element of medium volatility. Silicon has been used by Ahrens (1944) as an internal standard for the analysis of small amounts of iron in glass sands. Slavin (1941) has employed a "total energy" method for the same purpose. For both methods a standard deviation of about ±5% is reported.

Potassium. The most sensitive potassium line (K 7664) is situated in the red end of the spectrum and by its use concentrations as low as 0.0005% may be reached. However, K 4044 is quite often employed because of its more convenient wavelength. Using this line, a detection limit of about 0.01–0.02% is attainable, provided that CN emission is effectively quenched, as described in Section 10–2. The arc should be relatively cool, and consequently there should be a comparatively high concentration of one of the other alkali metals, which, if not already present in the specimen, may be added. Fast (1950) describes the use of K 4044–4047 in the presence of interference from Fe 4045. Use is made of the greater volatility of potassium to minimize interference, as in Section 12–2 and Section 6–4.

Sodium. Sodium is very sensitive. Provided that the so-called D lines (5895–5889) are used, 0.0001% or less may be detected. Na 5895 is more sensitive than Na 5889; the intensity ratio is two. More conveniently placed sodium lines are Na 3302.323 and 3302.988, which show adequate sensitivity for most purposes (detection limit about 0.001%). Interference may be encountered from the zinc line Zn 3302.588, but whether or not actual interference will occur in the presence of zinc depends on the dispersion of the spectrograph.

Like all alkali metals, sodium is relatively volatile. Its bright yellow color can be put to good use in timing the arc for some purposes (Section 5–11).

Magnesium. This element is extremely sensitive. Using Mg 2852, its most sensitive line, concentrations as low as ~0.0001% are usually detectable. Magnesium also has sensitive ion lines. See the discussions on calcium and titanium in this section for comments on relative sensitivities of ion and atom lines in different matrices.

Magnesium is generally of medium volatility. In silicates, it usually reaches its peak concentration in the arc shortly after the main volatilization of the alkali metals but before the main volatilization of aluminum and calcium.

Silicon. This extremely common element is rarely sought as a trace constituent in minerals, rocks, and soils. It is very sensitive and by using Si 2516 and Si 2881, the two most sensitive lines, concentrations of 0.001% and considerably less may be reached. Silicon is of medium volatility and in silicates it reaches its peak of volatilization after the alkali metals have distilled and before the major volatilization of aluminum has begun.

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WAVELENGTH TABLES

The most sensitive lines of the elements in the arc and possible interfering lines within ± 0.4-0.5A of each sensitive line.

Wavelengths, intensities, and symbols as given in the M. I. T. Wavelength Tables. Most sensitive arc and spark lines, as predicted from theory, are underscored with solid lines (————) and broken lines (– – – – –) respectively.

The following elements are included and are arranged alphabetically as follows: aluminum, antimony, arsenic, barium, beryllium, bismuth, boron, cadmium, calcium, cerium, cesium, chromium, cobalt, copper, dysprosium, erbium, europium, fluorine, gadolinium, gallium, germanium, gold, hafnium, holmium, indium, iridium, iron, lanthanum, lead, lithium, lutecium, magnesium, manganese, molybdenum, neodymium, nickel, niobium, osmium, palladium, phosphorus, platinum, potassium, praseodymium, rhenium, rhodium, rubidium, ruthenium, samarium, scandium, silicon, silver, sodium, strontium, tantalum, tellurium, terbium, thallium, thorium, thulium, tin, titanium, uranium, vanadium, wolfram, ytterbium, yttrium, zinc, and zirconium.

In accordance with the recommendation of the XVth Conference of the International Chemistry Union, element 74 has been referred to as wolfram and element 41 as niobium.

Subsequent to the preparation of these tables a valuable and much needed contribution has been published on the most sensitive lines on the rare earth elements (Smith and Wiggins, 1949). In this publication two sets of observations are given, one by the authors and the other by W. F. Meggers and B. F. Scribner. Their data are given in full at the end of the wavelength tables. At the head of the sensitivity column M and S, and S and W refer respectively to the two pairs of observers, Meggers and Scribner, and Smith and Wiggins. The numbers, 1, 2, 3 .... in the sensitivity columns refer to the order of sensitivity as found by each pair.

ALUMINUM (Al)

Ionization Potential, 5.96 Volts

Most Sensitive Lines	Excitation Potential
3961.527 I	3.13 Volts
3944.032 I	3.13 Volts
3092.713 I	4.0 Volts
3082.155 I	4.0 Volts

Eu	3961.99	10w
Mo	3961.988	3
U	3961.984	6
Tb	3961.970	3
Sm	3961.808	25
W	3961.760	5
Ce	3961.661	6
U	3961.660	1
Zr	3961.587	500
Yb	3961.544	30
Al I	3961.527	3000
Ru	3961.518	6
U	3961.515	8
Mo	3961.503	5
Ce	3961.386	2
Ag	3961.3	15
Pr	3961.284	10
Er	3961.210	6
Fe I	3961.145	25
Eu	3961.14	50w
U	3961.064	6
Re I	3961.033	30
Eu	3944.592	5w
Er	3944.423	12
Nd	3944.421	20
Ir I	3944.375	20
Re	3944.349	15
Th	3944.254	3
Tb	3944.20	6
Ru I	3944.190	10
Pr	3944.137	9
U	3944.130	8
Ni I	3944.126	5wh
Ce II	3944.093	8
Ir	3944.058	2
Al I	3944.032	2000
Rh	3944.019	5
Re	3944.016	15
Er	3944.014	2
Eu	3944.01	8h
Ce II	3943.888	40
U	3943.820	35
Pr	3943.753	10
Th	3943.694	10
Cb	3943.666	20
V I	3943.664	50
Tb	3943.66	8
Gd	3943.631	20
Sm	3943.621	8
Cr I	3943.614	18
Ce	3093.243	6
Tm	3093.12	30
V II	3093.108	100R
Dy	3093.108	15
Th	3093.055	12
U	3093.012	20
Ta	3092.994	18
Mg I	3092.991	125
Nd	3092.915	8
Cb	3092.886	1h
Al	3092.842	50R
Ce	3092.818	4
Fe	3092.778	50
Na II	3092.729	50
Ce	3092.724	4
V	3092.720	100r
U	3092.720	5
Al I	3092.713	1000
Yt	3092.712	8
Mo	3092.70	20
Sc II	3092.519	3
Ta	3092.444	50
Sc	3092.42	3
Ir	3092.401	5
Fe	3092.399	4
Cd II	3092.393	10
W	3092.285	7
Hf II	3092.245	20
Zr	3092.240	3
Co	3082.618	150R
Ti I	3082.615	6
U	3082.587	6
Tm	3082.57	10
Sc II	3082.56	2
V	3082.523	3
Dy	3082.515	15
Ta	3082.447	15h
Re I	3082.432	100w
Tb	3082.36	3
Ce	3082.304	20
Rb I	3082.27	10
Sm	3082.261	1
Mo	3082.220	4
Th	3082.176	10
Yt II	3082.167	4
Al I	3082.155	800
V	3082.111	80R
Er	3082.08	12
Mn	3082.052	50
Th	3082.031	12
U	3082.020	8
V I	3082.012	15
Gd	3082.000	100
Ce	3081.984	5
Mo	3081.950	25
W	3081.864	10
Ta	3081.850	50
Fe	3081.84	2
Cb	3081.769	1
U	3081.666	6

ANTIMONY (Sb)

Ionization Potential, Volts

Most Sensitive Lines	Excitation Potential
2877.915 I	5.3 Volts
2598.062 I	5.8 Volts
2528.535 I	6.1 Volts

Os	2878.400	40	Zr II	2877.551	4	O	2597.572	10
Mo	2878.382	20	Pt II	2877.520	40	Ru	2597.518	10
Tm	2878.36	10	Ti II	2877.436	30			
W	2878.30	1						
U	2878.240	5				Co I	2528.967	50R
Tm	2878.21	3	Ru	2598.581	20	W	2528.912	3
Ta	2878.20	4	Fe	2598.47	1	Fe	2528.879	2
Cb	2878.165	2	W	2598.421	10	Ru	2528.878	60
W	2878.079	4	Fe II	2598.369	700	Mo	2528.866	1
V	2878.022	2	Ir I	2598.284	8	V	2528.836	25
Ce	2878.018	2	Ce	2598.250	5	U	2528.77	5
Cr II	2877.978	30	Ta	2598.21	2s	Ru	2528.715	30
Sb I	2877.915	250W	Mn	2598.174	12	Mn	2528.702	12
			W	2598.107	6	Co II	2528.615	4
Ca	2877.91	1h	Rh	2598.072	4	Ta	2528.59	4
Eu	2877.890	2						
Dy	2877.885	2	Sb I	2598.062	200	Sb I	2528.535	300R
Cb	2877.852	2	Cb	2598.041	2			
Ru I	2877.840	3	Fe II	2598.028	4	Si I	2528.516	400
U	2877.830	2	Ir I	2598.000	2	Dy	2528.49	4
Eu	2877.76	5	Re	2597.964	20	V	2528.468	50
Cu II	2877.689	5	Ir	2597.862	3	Ce	2528.287	15
V	2877.688	15	Fe	2597.828	6	Cr I	2528.244	30
Ta	2877.686	15	W	2597.726	10	Fe	2528.174	6
Ir I	2877.678	20	U	2597.689	25	U	2528.099	10
U	2877.569	6	Rh I	2597.683	2	Ni I	2528.050	20

ARSENIC (As)

Ionization Potential, 10 Volts

Most Sensitive Lines	Excitation Potential
2860.452 I	6.6 Volts
2780.197 I	6.7 Volts
2349.84 I	6.6 Volts

Zr I	2860.851	15
U	2860.801	15
Rh I	2860.762	30
Dy	2860.70	2
W	2860.679	6
Pt II	2860.678	30
Rh I	2860.675	30
Ir I	2860.665	12
Ce	2860.643	2
Hf	2860.557	20
Ce	2860.555	3
Tm	2860.55	10
U	2860.466	35
As I	2860.452	50r
Yb	2860.40	1
Ru	2860.374	3
Hf II	2860.312	15
Ti I	2860.277	7
Er	2860.257	4
Fe	2860.21	2
Dy	2860.172	2
W	2860.163	5
Tm	2860.13	15
Os	2860.063	25
Ru I	2860.016	60
V I	2859.971	50

Cr I	2780.703	600R
Fe	2780.700	30
Fe	2780.54	10
Eu	2780.526	20
Bi I	2780.521	200w
Ir I	2780.409	3
W II	2780.283	10
Cb	2780.245	30
La II	2780.234	20
Ta	2780.208	4
As I	2780.197	75R
U	2780.040	8
Mo	2780.036	60
Ce	2780.005	15
Mn	2779.998	25
Mg	2779.834	40
Ce	2779.825	2
Sn	2779.817	80
La	2779.778	1

Co I	2350.280	12
Os	2350.23	30
Zr	2350.20	2
Ir	2350.054	15
Os	2350.04	12
Cb	2350.028	2
Ti	2349.94	3
Cd	2349.857	2
Sb	2349.853	8
U	2349.85	2h
Cu	2349.85	5
As I	2349.84	250R
W	2349.82	6
Os	2349.81	40
V	2349.806	3w
Mo	2349.78	10w
Yt	2349.70	8
Rh	2349.68	3
Ir	2349.662	5
Dy	2349.63	3
Re	2349.61	12
Zr	2349.59	10
Re	2349.40	12

BARIUM (Ba)

Ionization Potential, 5.19 Volts

Most Sensitive Lines	Excitation Potential
5535.551 I	2.23 Volts
4934.086 II	2.50 Volts
4554.042 II	2.73 Volts

Eu	5536.13	30
U	5535.796	6
La II	5535.671	50
Ba I	**5535.551**	**1000R**
Sm	5535.504	3
Nd	5535.476	3
Fe	5535.411	50
V I	5535.382	2
Tb	5535.38	15
Nd	5535.271	2
Ce	5535.240	15
Pr	5535.176	10
Gd	5535.16	8
Rh	5535.04	80
La II	4935.618	8
Yb	4935.502	200
Er	4935.498	35
Sm	4935.458	20
Pr	4935.380	2
bh Mg	4935.3	4
Co I	4935.222	2
Pr	4935.136	2
La II	4934.825	150
Ru	4934.607	4
Hf II	4935.45	40
Mn	4934.15	25
Th	4934.088	4
Ba II	**4934.086**	**400h**
Er	4934.074	18
Pr	4934.071	3
Co	4934.065	25
Fe I	4934.023	40
Ni I	4934.000	3
Th	4933.852	8
Dy	4933.845	2
W	4933.822	12
Re	4933.740	15w
Mo	4933.732	12
U	4933.657	8
Zr I	4933.643	4
Fe	4933.627	2
Ta	4933.527	5s
Ru I	4554.509	1000R
Pr	4554.498	2
Yt I	4554.459	3
Sm II	4554.443	60
Ce	4554.333	2
Dy	4554.234	2
Ba II	**4554.042**	**1000R**
Ce	4554.035	35s
Mo	4554.028	1
Zr II	4553.967	4
Cr	4553.949	20
U	4553.858	4
Th	4553.85	3
Cb	4553.836	5
Mo	4553.798	20
Hf	4553.776	10
Ce	4553.755	2
bh Pb	4553.7	6
Ta	4553.694	200 ℓ
W	4553.662	6
Yb	4553.561	20

BERYLLIUM (Be)

Ionization Potential, 9.28 Volts

Most Sensitive Lines	Excitation Potential
3321.343 I	6.43 Volts
3131.072 II	3.94 Volts
3130.416 II	3.94 Volts
2348.610 I	5.40 Volts

Eu	3321.857	30	U	3131.325	8	Ir	3130.285	4
U	3321.707	5	Tm	3131.26	400	Fe	3130.278	5
Ti II	3321.700	15	Ta	3131.216	5h	V II	3130.267	50
V I	3321.685	12	Cr	3131.211	20	La II	3130.25	3
Ti I	3321.588	15	Os	3131.115	125	Sm	3130.235	5
W	3321.565	8	Zr I	3131.110	7	Ce	3130.197	15
V	3321.538	3	Be II	3131.072	200	Ti I	3130.175	2
Re	3321.462	10	Er	3131.07	3	Dy	3130.159	4
Th	3321.453	10	Th	3131.070	12	W	3130.155	5
Nd	3321.395	8	Ho	3130.99	6	Zr I	3130.063	3
Be I	3321.343	1000r	Ce	3130.919	5	Ag	3130.009	25h
Ce	3321.275	3	Ce	3130.872	30			
Ru	3321.254	12	Gd	3130.814	3	Bi I	2349.10	10
Ni I	3321.242	4	Ti II	3130.800	25	U	2348.91	2
Mo	3321.196	1	Rh I	3130.790	60	La II	2348.86	2h
Cr	3321.19	20	Cb	3130.786	100	Mo	2348.84	3
Sm II	3321.184	50	Eu	3130.74	100W	Mn	2384.83	3
Tb	3321.15	30	U	3130.732	10	Cu II	2348.82	15d
W	3321.133	6	Ir	3130.578	3	Re	2348.80	9
Be I	3321.086	100	Ta	3130.578	100W	Cb	2348.748	3w
Be I	3321.013	50	Ba I	3130.570	2	Ni I	2348.74	10
Pd I	3320.987	15	Fe II	3130.567	4	Os	2348.61	3
Ce II	3320.940	10	Cr	3130.565	1	Be I	2348.610	2000R
U	3320.92	1	Ce	3130.516	5	Zr	2348.586	15
Mo	3320.902	3	W	3130.456	10	W	2348.56	2h
Ce	3131.505	2d	Be II	3130.416	200	Pt II	2348.548	3
Os	3131.481	20	Ti I	3130.376	2	Ru	2348.327	50
Fe	3131.455	2h	U	3130.373	3h	Fe II	2348.303	5
Tb	3131.35	8	Ce	3130.334	30	Ir	2348.301	20
			Ta	3130.29	15ℓ	W	2348.151	8

BISMUTH (Bi)

Ionization Potential, Volts

Most Sensitive Lines	Excitation Potential
4722.552 I	4.02 Volts
3067.716 I	4.02 Volts
2897.975 I	5.60 Volts

Mo	4723.063	10
Sm	4722.947	3h
Ta	4722.877	200
V I	4722.865	20
Bi I	4722.831	10
U	4722.726	40
Er	4722.703	12
Pr	4722.670	5
Sm	4722.632	3h
Ti I	4722.616	80
Bi I	4722.552	1000
Sr I	4722.278	30
Bi I	4722.190	10
Zn I	4722.159	400w
Th	4722.109	2
Fe	3068.176	150
Zr II	3068.024	2
Mo	3067.997	30
Fe	3067.944	15
Ir	3067.939	2h
Ce	3067.895	6
W	3067.866	3
Eu	3067.784	7
U	3067.758	8
Sn	3067.755	10
Th	3067.734	12
Bi I	3067.716	3000hR
Sm	3067.672	15
Eu	3067.672	8
Mo	3067.642	10
W II	3067.568	3
Ce	3067.443	4
Hf	3067.414	30
W II	3067.41	2
Re I	3067.390	60
Rh	3067.305	80
Fe I	3067.244	300
Ta	2898.425	30
Mo	2898.386	2
U	2898.366	4
Fe	2898.355	100
Ir I	2898.350	10
Ce	2898.336	6
Be I	2898.27	20
Th	2898.267	4
Hf I	2898.259	50
Zr	2898.256	4
W	2898.253	8
Be I	2898.19	15
Fe	2898.06	2
U	2898.013	6
Mn	2897.990	15
Bi I	2897.975	500WR
V	2897.896	1
Pt I	2897.873	400
Fe	2897.85	2
Cb	2897.812	15
Mn	2897.797	15
La II	2897.76	2
Ru	2897.715	6
Cr	2897.704	3
Yt II	2897.676	3
Ir	2897.653	3
Fe	2897.64	4
U	2897.636	3h
Rh	2897.633	2
Mo	2897.628	20
Re	2897.592	10d
Er	2897.518	12

BORON (B)

Ionization Potential, 8.28 Volts

Most Sensitive Lines	Excitation Potential
2497.733 I	4.9 Volts
2496.778 I	4.9 Volts

V	2498.044	7	Fe	2496.991	20
Ge I	2497.963	8	Hf II	2496.986	30
Mo	2497.863	20	Cb	2496.973	1
Fe II	2497.820	15	Ta	2496.957	2
B I	2497.733	500	B I	2496.778	300
Sn	2497.720	8	Sn	2496.768	10
Fe II	2497.717	1	Re	2496.70	20
Ru	2497.678	50	W II	2496.638	10
V I	2497.655	4h	Ta	2496.635	20
Th	2497.59	3	Fe	2496.533	40
Mo	2497.580	30h	Zr II	2496.480	2
Co	2497.501	1	Gd	2496.40	2
W II	2497.484	10	Cr I	2496.309	125r
W	2497.292	5	Ir I	2496.271	10
V I	2497.099	2	Ta	2496.237	2h

CADMIUM (Cd)

Ionization Potential, 8.96 Volts

Most Sensitive Lines	Excitation Potential
3466.201 I	7.3 Volts
3261.057 I	3.78 Volts
2288.018 I	5.4 Volts

Ce	3466.646	2	Pt I	3261.072	3
Tb	3466.57	8	Cd I	3261.057	300
Th	3466.536	5	Ir I	3260.998	2h
U	3466.503	3	Ce II	3260.975	25
Fe I	3466.500	30	Ca	3260.93	1h
Eu	3466.416	30	Th	3260.922	8
U	3466.30	8	Zr	3260.916	2h
Pr	3466.237	2	Eu	3260.883	5
Cd I	3466.201	1000	Tb	3260.83	15
U	3466.139	4	Co I	3260.819	70
Dy	3466.12	2	B II	3260.74	4
Ce	3466.077	5	Dy	3260.69	10
Ce	3466.029	3	Nd	3260.655	10
Re I	3465.983	20	Os	3260.568	15
Tb	3465.98	30			
Th	3465.929	5			
Hf II	3465.92	5	Rh	2288.57	25
Cb	3465.865	30	Mn	2288.42	6
Fe I	3465.863	500	Ni I	2288.39	12
Mo	3465.86	5	Pt II	2288.192	15
Co I	3465.800	2000R	Sb	2288.139	5
Th	3465.766	10	As I	2288.12	250R
			V	2288.095	3h
Yb	3261.509	5	Cd I	2288.018	1500R
Fe	3261.333	25			
Ce II	3261.242	8	Ir	2287.878	20
Dy	3261.22	5	Ta	2287.84	5
W	3261.165	10	Co	2287.809	12d
Ru	3261.129	30	Ru	2287.68	60
Ce	3261.116	2	W	2287.67	10
Th	3261.11	5	Ni II	2287.65	2
V	3261.081	15	Fe I	2287.630	5
Zr I	3261.078	2h	Ru	2287.525	3

CALCIUM (Ca)

Ionization Potential, 6.09 Volts

Most Sensitive Lines	Excitation Potential
4226.728 I	2.92 Volts
3968.468 II	3.11 Volts
3933.666 II	3.14 Volts

U	4227.330	6
Gd	4227.145	50
Mo	4227.085	3
Nd	4226.992	6
W	4226.915	15
Cr	4226.758	125
Ir	4226.735	30
Ce	4226.734	50
Ca I	4226.728	500R
Yt	4226.726	5
Mo	4226.726	15
Ru I	4226.656	15
Ir	4226.628	5
V I	4226.624	8
U	4226.60	1
Ge I	4226.570	200
Mo	4226.549	10
Os	4226.527	12
Tb	4226.44	50
Fe I	4226.430	80
W	4226.343	10
Ce	4226.335	2
Mo	4226.291	20
Cb	4226.247	4

Th	3969.003	10
Nd	3968.876	20
Eu	3968.870	3wh
Mo	3968.748	8
Tb	3968.73	2
Zr	3968.723	3
W	3968.590	6
Ir	3968.475	25
Cb	3968.471	3
Ce	3968.469	35
Ca II	3968.468	500R
Lu	3968.464	50
Ru	3968.461	12
Yt	3968.43	10
Dy	3968.395	300
U	3968.374	1
Fe	3968.370	2
Gd	3968.35	20
Zr I	3968.257	100
Ag	3968.22	100
W	3968.171	8
Rh I	3968.164	2
Ta	3968.16	4h
Pr	3968.158	25
Tb	3968.146	2
V II	3968.094	25
Hf	3968.01	5
U	3968.007	6h
Fe I	3967.969	60

Nd	3934.093	20
Ce	3934.076	6
V I	3934.013	100
U	3933.985	6
Co I	3933.914	60
Tb	3933.905	4
Ir	3933.901	20
Ce	3933.731	60
Ru	3933.680	5
Eu	3933.677	10
Ca II	3933.666	600R
Hf II	3933.664	20
Ir	3933.664	20
U	3933.662	2
Co	3933.654	80
Ag	3933.62	80
Fe I	3933.605	200
Sm II	3933.592	200
Tb	3933.469	6
Cb	3933.394	3
Sc I	3933.381	60
Pr	3933.300	9
Zr I	3933.178	9

CERIUM (Ce)*

Ionization Potential, Volts

Most Sensitive Lines	Excitation Potential
4296.680 II	2.87 Volts
4222.599 II	2.92 Volts
4186.599 II	3.33 Volts

Gd	4297.179	100	Na I	4222.8	3
U	4297.112	18	U	4222.739	6
Cr I	4297.050	100	Cr I	4222.732	100
Ir	4297.030	3	Tb	4222.71	9
Ni I	4296.984	2	Tm	4222.67	10
Gd	4296.90	4	Ce II	4222.599	80
Sr	4296.82	3	Mo	4222.411	20
Ce	4296.786	5	U	4222.375	18
Rh I	4296.770	40	Eu	4222.31	5
Er	4296.752	10d	Ho	4222.26	3
Sm	4296.750	100	Dy	4222.221	10
Zr II	4296.742	3	Fe I	4222.221	200
Ru	4296.689	7	P	4222.15	300
Ce II	4296.680	40			
Cr	4296.631	15	Fe I	4187.044	250
Mo	4296.624	15	U	4186.977	10
Fe II	4296.585	2	Ce	4186.860	2
Pr	4296.55	15	Ho	4186.84	3
Hf	4296.41	10	Dy	4186.810	100w
Ce	4296.371	10	U	4186.790	6
Nd	4296.363	12	Zr I	4186.777	3
Tb	4296.35	20	Er	4186.71	8
Dy	4296.34	2	Zr II	4186.688	3
Gd	4296.291	40	Tb	4186.60	2
Cr	4296.275	15	Ce II	4186.599	80
Os	4296.218	12	U	4186.477	6
Pr	4296.18	10	Eu	4186.42	6
			Pr	4186.395	12
Sm	4223.056	3	Cr	4186.359	50
Gd	4222.98	10	Nd	4186.311	25
Pr	4222.98	125	Tm	4186.31	5
Mo	4222.961	15	Mo	4186.281	15
U	4222.94	1	Ir	4186.280	2
Tb	4222.91	6w	Tb	4186.24	10
Ce	4222.884	3	Ti I	4186.123	100

*See list of sensitive rare earth lines at end of tables.

CESIUM (Cs)

Ionization Potential, 3.87 Volts

Most Sensitive Lines	Excitation Potential
8943.50 I	1.38 Volts
8521.10 I	1.45 Volts
4593.177 I	2.69 Volts
4555.355 I	2.71 Volts

Fe I	8945.204	20
Re	8944.56	2
Cs I	8943.50	2000R
Fe I	8943.00	3
Zr I	8941.74	3
Ba I	8521.96	2
Mn I	8521.57	10h
Cs I	8521.10	5000R
Ti I	8518.32	100
Mo	4593.643	8
Pr	4593.571	8d
Sm II	4593.531	50
Sm	4593.407	2
Yb	4593.37	4
Th	4593.290	3
Ru I	4593.213	7
Cs I	4593.177	1000R
Ce	4593.103	3
Tb	4593.06	3
Ru	4593.025	6
Sc I	4592.939	2
U	4592.933	3
Er	4592.93	3
Fe I	4592.655	200
Fe II	4555.895	12
Th	4555.815	3
Eu	4555.71	12W
Er	4555.693	3
Ce	4555.620	2
Cb	4555.561	3h
Zr I	4555.52	30
Ti I	4555.489	125
Ce	4555.425	5
Eu	4555.38	4
Cs I	4555.355	2000R
W	4555.327	7
Yt I	4555.298	2
Cr	4555.296	15
Tm	4555.26	25
Dy	4555.24	4
Nd	4555.140	15
Zr I	4555.130	15
U	4555.095	20
Cr	4555.092	15
Ti I	4555.083	12
Th	4555.071	3
Gd	4554.99	6
Nd	4554.967	5
Cr	4554.830	25

CHROMIUM (Cr)

Ionization Potential, 6.74 Volts

Most Sensitive Lines	Excitation Potential
4289.721 I	2.88 Volts
4274.803 I	2.89 Volts
4254.346 I	2.90 Volts

Mo	4290.184	30h	W	4274.938	10
Ho	4290.17	2	Os	4274.905	9
W	4290.144	8	Cb	4274.892	5
Mn	4290.112	8	Cr I	4274.803	4000R
Gd	4290.067	6	Zr I	4274.769	9
Ce	4289.938	50	Cb	4274.689	5
Ti I	4289.919	15	Ti I	4274.584	100
Gd	4289.901	40	W	4274.550	20
Pr	4289.89	15	Ti I	4274.400	5
U	4289.882	12	Tb	4274.36	2h
Tb	4289.73	30			
Cr I	4289.721	3000R			
U	4289.556	4	Ce	4254.905	8
Ce II	4289.454	25	Yb	4254.77	4
Cb	4289.444	10	N I	4254.75	15
Pr	4289.42	12	Ce	4254.701	20
Mo	4289.415	20	Cb	4254.694	10
Sm	4289.365	15	Th	4254.458	8
Ca I	4289.364	35	Ho	4254.43	100
Nd	4289.363	15	Mo	4254.429	10
Dy	4289.35	2	V II	4254.425	3
W	4289.291	1	Pr	4254.420	35
Ti I	4289.073	125	Cb	4254.392	10
			Ce	4254.370	8
			Cr I	4254.346	5000R
Pr	4275.32	5	Er	4254.32	7
Tb	4275.21	15	W	4254.288	4
Pr	4275.17	12	Bi I	4254.152	10
W	4275.149	6	W	4254.060	8
Cu I	4275.131	80	Gd	4254.03	3
Nd	4275.083	20	Ce	4254.004	3
Co I	4275.069	3	Tb	4254.00	5
U	4275.02	2	Fe	4253.93	2
Dy	4275.00	5	Th	4253.875	6
Pr	4274.959	3			

COBALT (Co)

Ionization Potential, 8.5 Volts

Most Sensitive Lines	Excitation Potential
3453.505 I	4.00 Volts
3405.120 I	4.05 Volts

Th	3453.922	4	Th	3405.561	3
Eu	3453.88	2w	Ce	3405.444	6
Pt	3453.86	1	Cb	3405.411	80
Pr	3453.784	6	Bi	3405.326	40
U	3453.780	4	W	3405.277	7
Ce	3453.760	3	Ru	3405.277	3
Cr I	3453.743	30	Cr	3405.22	12
Tm	3453.66	150	Mo	3405.204	8
Ti I	3453.654	3	V I	3405.160	30
Ce	3453.639	2	Co I	3405.120	2000R
U	3453.570	5	Ti I	3405.094	20
Sm	3453.547	15	Ag	3405.03	3
Ti I	3453.531	5h	Dy	3404.99	4
Co I	3453.505	3000R	V I	3404.960	8
Re I	3453.502	40	U	3404.933	3
Eu	3453.47	3	Ce	3404.910	18
Tb	3453.46	15	Mo	3404.864	6
Cr I	3453.328	35	Zr II	3404.832	40
Re	3453.285	20	W	3404.803	8
Ce	3453.241	8	Sm	3404.767	2
Sm	3453.226	4	Nd	3404.763	4
La II	3453.168	50	Fe I	3404.754	2
Ho	3453.13	30	Re I	3404.724	100
Dy	3453.12	5wh	Tb	3404.71	3
Er	3453.10	12	Th	3404.654	4
Os	3453.054	20s			

COPPER (Cu)

Ionization Potential, 7.68 Volts

Most Sensitive Lines	Excitation Potential
3273.962 I	3.77 Volts
3247.540 I	3.80 Volts

Fe	3274.453	80	Ce	3247.898	3
Th	3274.399	6	Tb	3247.79	8
Eu	3274.29	3	U	3247.709	4
Tb	3274.24	70	Ir I	3247.667	3
Na II	3274.220	15	Mo	3247.621	30
Ce	3274.112	8	Ce	3247.552	15
Ce	3274.064	10	Ag	3247.55	15
Ti I	3274.047	7	Sb	3247.547	2h
Ce	3273.964	5	Mn	3247.542	125
Cu I	3273.962	3000R	Cu I	3247.540	5000R
Mo	3273.961	20	Eu	3247.530	50W
Ca	3273.958	2	Er	3247.52	18d
Co	3273.931	10	Cb	3247.474	50w
Ce	3273.926	5	Sm	3247.366	4
Cb	3273.886	20r	Eu	3247.30	4
Th	3273.884	10	Fe I	3247.278	20
Hf II	3273.655	20	Cr I	3247.274	20
Ru	3273.621	2	Ce	3247.250	3
Sc I	3273.619	35	Fe	3247.213	10
U	3273.596	5	U	3247.209	2
Ce	3273.516	4	Tb	3247.18	15
			Co I	3247.179	80
			Sm	3247.17	1
			Ce	3247.118	3
			La I	3247.04	8

DYSPROSIUM (Dy)*

Ionization Potential, Volts

Most Sensitive Lines

4211.719
4000.454

Excitation Potential

Tb	4212.23	3w	Eu	4000.807	3
Zr I	4212.158	3	Ce	4000.799	4
Ru I	4212.063	125	U	4000.732	6
Cb	4212.040	4	Eu	4000.698	3
Gd	4212.019	150	W	4000.694	12
Ce	4211.906	1	Ce	4000.675	5
Zr II	4211.875	18	Cr	4000.63	5
Cu II	4211.861	1h	Ho	4000.62	4
Pr	4211.858	50d	Cb	4000.605	2
Os	4211.855	150	Nd	4000.562	8d
Mn	4211.748	30	Mo	4000.497	8
Ho	4211.73	5	Nd	4000.493	10d
Ti I	4211.728	30	Pr	4000.478	8
Tb	4211.72	25	Tb	4000.46	15
Dy	4211.719	200	Dy	4000.454	400
Er	4211.718	30	Fe	4000.452	35
U	4211.68	10	Er	4000.452	35
U	4211.620	18	Ho	4000.45	5
Ce	4211.582	3	Mo	4000.386	6
Th	4211.519	8	Th	4000.287	8
Cr	4211.349	100	Fe I	4000.266	8
Zr	4211.335	12	Pr	4000.190	50
U	4211.310	10	Gd	4000.16	10h
Nd	4211.286	30	V I	4000.078	8
Dy	4211.248	4			
Pr	4211.24	5			

*See list of sensitive rare earth lines at end of tables.

ERBIUM (Er)*

Ionization Potential, Volts

Most Sensitive Lines

4007.967
3906.316
3692.652

Excitation Potential

Ce	4008.446	6	Hf	3906.89	3	Ta	3693.047	35r
Nd	4008.416	5	Sm II	3906.805	6	Fe	3693.032	15
Gd I	4008.331	15	Th	3906.796	8	Tb	3692.95	30
Sm	4008.330	8	Fe	3906.751	10	U	3692.91	5
Cb	4008.280	5	V I	3906.748	50	Sm	3692.899	10
Ru I	4008.269	20	Tb	3906.53	4	Mn	3692.812	50
Th	4008.216	10	Fe I	3906.482	300	Nd	3692.768	12
Er	4008.185	8	Mo	3906.480	5	Sm	3692.763	20
V I	4008.169	2	Ce	3906.452	8	U	3692.750	10
Sm II	4008.091	10	Hg I	3906.410	25	W	3692.725	7
Ti I	4008.062	50				Ir I	3692.694	15
Mo	4008.054	4	Er	3906.316	25	Eu	3692.66	5w
Ir I	4008.052	12	Co I	3906.294	150			
Mn	4008.020	15	Pt I	3906.291	2	Er	3692.652	20
Eu	4007.98	6	Ho	3906.26	3	Fe	3692.652	5
			Zr	3906.151	3	Ho	3692.65	10
Er	4007.967	35	Ce	3906.104	2	Mo	3692.645	3
			Nd	3906.096	15	Zr II	3692.635	2
Ho	4007.96	4	Pr	3906.093	6	Th	3692.571	10
Co I	4007.943	3	Fe II	3906.037	2w	Ce	3692.552	2
U	4007.934	8	Ba I	3906.010	4	Yt I	3692.529	7
Pr	4007.78	8	Ru	3905.991	6	Ru	3692.370	6
Dy	4007.77	12	W	3905.970	8	Rh I	3692.357	500hd
Tb	4007.75	3	Dy	3905.95	6	Pr	3692.293	4
U	4007.689	2	Ce	3905.920	3			
Eu	4007.687	5d	U	3905.896	8			
La	4007.662	3	Nd	3905.886	40			
Zr I	4007.601	25						
Ce	4007.588	15						
Ru	4007.535	20						

*See list of sensitive rare earth lines at end of tables.

EUROPIUM (Eu)*

Ionization Potential, 5.64 Volts

Most Sensitive Lines	Excitation Potential
4594.02 I	2.69 Volts
4205.046 II	2.93 Volts
3907.11 II	3.36 Volts

Pr	4594.572	3
Nd	4594.447	10
Cr	4594.403	10
Tb	4594.31	2
U	4594.294	6
Ce	4594.129	4
Mn	4594.108	12
V I	4594.108	30wh
Eu	4594.02	500R
Er	4594.01	2
Yt	4594.00	3
Tb	4593.947	4
Nd	4593.936	2h
Ce	4593.932	30
Pr	4593.926	30
bh La	4593.9	5
Cr	4593.831	12
Ce	4593.716	2
Mo	4593.643	8
Pr	4593.571	8d
Fe	4205.546	50
Sm	4205.361	8
Cb	4205.311	15
Nd	4205.255	5
Tb	4205.23	2
Os	4205.222	9
Sc I	4205.194	10
Ce	4205.161	6
bh Ca	4205.1	6
V II	4205.086	5
Eu II	4205.046	200R
Dy	4205.03	7
Eu	4204.909	5
Gd	4204.839	25
Sm II	4204.813	8
Mo	4204.809	25
Ce	4204.739	15
Yt II	4204.696	15
Mo	4204.609	15
Pr	4204.58	5
Os	4204.560	12
Ag	3907.59	3
U	3907.558	6
Sc I	3907.476	125
Fe	3907.470	15
Ce	3907.445	6
Th	3907.342	8
Pr	3907.296	8
Ce	3907.289	35
W	3907.202	6
V	3907.17	2h
Gd	3907.125	100W
Sm	3907.124	10
Eu II	3907.110	1000RW
U	3907.018	5
Mo	3906.976	5
Ce	3906.924	8
Mo	3906.916	5
Cb	3906.906	5
Hf	3906.89	3
Sm II	3096.805	6
Th	3906.796	8
Fe	3906.751	10
V I	3906.748	50
Tb	3906.53	4
Fe I	3906.482	300

*See list of sensitive rare earth lines at end of tables.

FLUORINE (F)

Ca F:	5291.0	(head)
	5292.9	
	5296.8	
	5298.6	

and other components of the same sequence.

Sr F:	5772.0	(head)
	5779.5	

and other members of the same sequence.

Either Ca F or Sr F bands can be used. Usually the heads are employed, but if they have interference other band components can be used.

GADOLINIUM (Gd)*

Ionization Potential, Volts

Most Sensitive Lines	Excitation Potential
4262.095 II	3.62 Volts
4251.736 II	3.28 Volts
3646.196 II	3.62 Volts

Tb	4262.59	2
Ce	4262.367	2
Cr	4262.356	30
La I	4262.334	15
Pr	4262.314	10
W	4262.269	7
Nd	4262.239	15
Eu	4262.177	2
V I	4262.161	20
U	4262.155	6
Cr	4262.133	40
Gd II	4262.095	150
Cb	4262.053	20
Ir	4261.888	10
Nd	4261.837	20
Tb	4261.83	8
bh Ca	4261.8	2
Pr	4261.796	15
Eu	4261.794	4
Cb	4261.714	5
Cr	4261.615	35
Cr I	4252.243	35
Ni I	4254.107	2
Pr	4252.07	4
Er	4251.938	18
Mo	4251.873	60
Ce	4251.858	10
Sm II	4251.788	200
Ti I	4251.761	10
Gd II	4251.736	300
Dy	4251.73	7
Tb	4251.72	12
Ti I	4251.606	20
Ce	4251.602	8
Pr	4251.490	40w
Yb	4251.489	15
Mo	4251.389	5
Ce	4251.364	5
Tb	4251.33	10
U	4251.326	10
Sm	4251.303	2
Yt I	4251.205	25
Eu	3646.660	10W
Ce	3646.652	10
Re	3646.628	10
Dy	3646.60	5
W II	3646.525	10 ℓ
U	3646.491	2
Tb	3646.46	8
Pr	3646.299	50
U	3646.217	10
Ti I	3646.200	70
Gd II	3646.196	200w
Cr	3646.161	18
Ru	3646.114	2
Sm	3646.013	2
bh Sr	3646.0	4
Pd I	3646.968	15
Er	3645.938	15
Cb	3645.929	1
Sm II	3645.898	4
Dy	3645.86	6
Fe	3645.825	80
Sm	3645.789	5d
Nd	3645.776	8
Ce	3645.711	2
Pr	3645.660	30

*See list of sensitive rare earth lines at end of tables.

GALLIUM (Ga)

Ionization Potential, 5.97 Volts

Most Sensitive Lines	Excitation Potential
4172.056 I	3.06 Volts
4032.982 I	3.06 Volts
2943.637 I	4.3 Volts

Ir I	4172.559	150
La I	4172.316	8
Pr	4172.273	75
Ho	4172.23	2
Yb	4172.23	2
U	4172.18	3
Ce II	4172.161	18
Fe	4172.127	80
Ga I	4172.056	2000R
Dy	4171.992	15
Ce	4171.964	2
Dy	4171.925	4
Ti II	4171.903	15
Pr	4171.824	75
Tb	4171.80	8
Ce	4171.769	2
Gd	4171.71	25
Er	4171.708	15
Fe	4171.700	8
Cr	4171.675	70
U	4171.591	30
Gd	4033.491	10
U	4033.427	12
Ce	4033.378	2h
Re I	4033.307	40
Cr I	4033.263	30
Pr	4033.24	3
Cb	4033.203	5
Sr I	4033.191	6
Mn I	4033.073	400r
Cr	4033.072	15
Ta	4033.069	100
In	4033.066	4
Tb	4033.04	125
Ga I	4032.982	1000R
Sm	4032.977	20
Pr	4032.974	15
V I	4032.856	2
Dy	4032.847	8
Ce	4032.748	2
Tb	4032.705	3
Ti I	4032.632	35
Fe I	4032.630	80
Tb	4032.626	4
Ce	4032.554	3
Th	4032.54	10
Cb	4032.524	30
Ga	2944.175	10
Er	2944.071	12
Ce	2943.987	6
W	2943.959	5
Ru	2943.921	50
Ni I	2943.914	50r
Mn	2943.908	2
U	2943.895	10
Ir	2943.87	4d
V I	2943.827	7h
Sm	2943.786	8
Ta	2943.769	10
Ir	2943.725	3h
Ce	2943.673	8
Ga I	2943.637	100*
V	2943.636	2
Ir	2943.628	3h
Fe	2943.57	12
La II	2943.551	2
Nd	2943.500	3
Sm	2943.492	8
Co I	2943.484	30
Ru I	2943.481	30
U	2943.405	6
Mo	2943.380	1
Re I	2943.380	15
Tm	2943.36	6
W	2943.326	7
Ir	2943.260	4
Ce	2943.215	6
V I	2943.196	30

*The M.I.T. tables assign an intensity value of "10" to Ga 2943, which is a sensitive line much used by spectrochemists. Because this very low intensity value may be misleading, an intensity of "100" is given above.

GERMANIUM (Ge)

Ionization Potential, 8.09 Volts

Most Sensitive Lines	Excitation Potential
3269.494 I	4.65 Volts
3039.064 I	4.94 Volts
2651.178 I	4.8 Volts

Fe	3269.959	5	Ca I	3039.21	1h
Sc I	3269.904	30	Cb	3039.187	2
Os	3269.887	8	U	3039.136	5
U	3269.779	10	Sm	3039.128	15
Eu	3269.66	4wh	Ge I	3039.064	1000
Zr I	3269.657	12	Ce	3038.993	4
W	3269.628	10ℓ	Nd	3038.962	4
Dy	3269.527	2	Ru	3038.784	3
Ge I	3269.494	300	Ti II	3038.706	2
Th	3269.469	10	V	3038.706	20
U	3269.458	2	Ho	3038.69	4
Eu	3269.414	2	Tb	3038.66	8
Er	3269.411	18	Mn	3038.602	3
Fe	3269.235	20	Th	3038.600	12
U	3269.229	2			
Os	3269.209	200			
Ta	3269.140	70r	Fe I	2651.706	60
Ce	3269.129	10	Ge I	2651.575	30
Dy	3269.12	20	Ru	2651.507	20
Cb	3269.117	2	Ta	2651.483	50
Ca I	3269.101	10	W	2651.441	9d
Re	3269.037	30	Ce	2651.418	2
			Ru I	2651.292	60
U	3039.501	10	Ge I	2651.178	400*
Cb	3039.406	3	Hf II	2651.165	15
Sm	3039.358	6	Cb	2651.122	3
In I	3039.356	1000R	W	2651.023	1
Fe	3039.316	20	Ce	2651.006	25
W	3039.311	10	Pt I	2650.857	700
U	3039.263	15	Be I	2650.781	25
Ir I	3039.260	25	Yb	2650.74	2
Ce	3039.253	4	W	2650.711	2

*An intensity value of "40" for Ge 2651 listed in M.I.T. tables seems low, and an approximate value of "400" is given here.

GOLD (Au)

Ionization Potential, 9.2 Volts

Most Sensitive Lines	Excitation Potential
2675.95 I	4.6 Volts
2427.95 I	5.1 Volts

U	2676.410	4	Mn	2428.422	12
Ce	2676.355	2	Fe II	2428.361	3
Ru	2676.353	50	Ir I	2428.360	2
Mn	2676.331	15	Ti I	2428.359	8
Rh	2676.25	1	Co II	2428.293	10
Ru	2676.190	8	Fe II	2428.286	1
Cb	2676.125	2	V I	2428.279	30r
Ce	2676.121	2	Ti I	2428.228	15
Fe	2676.11	15w	Pt I	2428.203	100
Rh I	2676.110	10	Fe	2428.20	9
Ti I	2676.080	6	Ag II	2428.196	1
Co I	2675.982	10w	W	2428.173	5
V I	2675.973	6	Sr I	2428.095	10h
Au I	2675.95	250R	Pt I	2428.035	100
			Th	2427.99	3
Cb	2675.944	10	Ir	2427.963	5
Ta	2675.901	150	Au I	2427.95	400R
U	2675.880	15			
W	2675.869	12	Os	2427.900	8
V I	2675.761	12	W II	2427.813	1
Ce	2675.733	2	V I	2427.745	6
Cr	2675.682	1	Ru	2427.741	2
Th	2675.670	8	Ta	2427.642	150
La II	2675.655	2	U	2427.622	12
Ta	2675.54	2	Ir I	2427.613	25
W	2675.400	10	Cb	2427.539	5
			W II	2427.490	10d

HAFNIUM (Hf)

Ionization Potential

Because of a lack of information on the spectrochemical analysis of traces of Hf, it has not been possible to list the most sensitive lines of Hf with certainty. Several sensitive lines have been given by authors, but little has been said about the most sensitive. Petersen (1927)[1] examined the lines of Hf between 2500 - 3500 A, and reported the ion line at 2773.357 A as the most sensitive, and 2866.373 and 2919.594 as the next most sensitive: other persistent lines reported were 2516.881, and 2887.135, 2898.259, 2904.408, 2904.751, 2940.772, 2964.876 and 3194.193. De Rubies and Agaudo (1935)[2] give in addition to 2516, 2773, 2898, 2904, 2940, the following lines; 2513.028, 2641.406, 2820.224, 2916.481, 3072.877, 3134.718 and 4093.161. Meggers (1928)[3] has also given a list of sensitive lines, most of which have been listed above.

[1] Peterson, M., Nature, 119, 352-353, 1927.

[2] De Rubies, S. P., Agauda, J. G., Annales, Soc. Espan. Fis. Quim., 33, 549, 1935.

[3] Meggers, W. F., U. S. Bur. Stds. Jour. Res., 1, 151-187, 1928.

HOLMIUM (Ho)*

Ionization Potential, Volts

Most Sensitive Lines Excitation Potential

3891.02
3748.17

Eu	3891.48	3w	Cr I	3748.614	40
Ru	3891.410	20	Ir I	3748.564	3
Re	3891.398	15	Cb	3748.554	10
Zr I	3891.383	100	Ce	3748.527	2
Eu	3891.34	4w	Sm	3748.515	5
Cb	3891.300	50	Pr	3748.505	5
W	3891.249	9	Fe II	3748.490	2h
V I	3891.220	8	Mo	3748.490	15
Sm II	3891.179	50	Ca I	3748.374	12
V	3891.119	5	Th	3748.304	10
U	3891.090	10	Fe I	3748.264	500
Yt	3891.083	2h	Rh I	3748.217	200
Th	3891.060	10	Ho	3748.17	60
Ho	3891.02	200	Sm	3748.153	5
Ce II	3890.986	12	Mo	3748.13	1
Tb	3890.95	5	Ti I	3748.102	10
Nd	3890.940	20	Pr	3748.058	9
Gd	3890.884	15	Ce	3748.056	10
Yt	3890.858	4	Ti II	3748.003	2
Fe	3890.844	60	La	3747.99	2
Ce	3890.761	8	V I	3747.982	50
Cb	3890.749	2	Dy	3747.827	60
W	3890.741	7	Ti I	3747.782	7
Ta	3890.714	2	Sm	3747.753	3
Mo	3890.706	5	Tb	3747.64	30
Er	3890.619	10			
Ba I	3890.583	3			
Nd	3890.580	30			
Ce II	3890.527	4			
Tm	3890.52	40			

*See list of sensitive rare earth lines at end of tables.

INDIUM (In)

Ionization Potential, 5.76 Volts

Most Sensitive Lines	Excitation Potential
4511.323 I	3.01 Volts
3256.09 I	4.10 Volts

Nd	4511.823	50	Ru I	4511.197	25	Th	3256.273	10
Pr	4511.815	3	Ti	4511.170	40	Ce	3256.251	12
U	4511.746	5h	Zr I	4511.170	5	Dy	3256.25	25
Er	4511.715	4w	U	4511.158	4	Ce	3256.232	6
Ce	4511.635	10	Pr	4511.091	3	W	3256.230	8
Eu	4511.53	3w	Cb	4511.089	5	Mo	3256.210	40
Tb	4511.52	40	Ta	4510.982	200W	Mn	3256.137	75
Ta	4511.503	300	Ce	4510.921	6			
Pr	4511.455	5	Er	4510.917	2w	In I	3256.09	1500R
V I	4511.432	2	Ho	4510.81	2	W	3255.962	9
Pr	4511.349	4				Pt I	3255.916	3
Cd	4511.34	5				Fe II	3255.890	20
In I	4511.323	5000R	La	3256.601	3	Sm	3255.843	6
			V	3256.46	8	Ca	3255.811	1h
Sm	4511.307	40	U	3256.458	2	Re	3255.801	4
Sn	4511.30	200	Pt	3256.433	2	Er	3255.787	10
Nd	4511.290	25	Er	3256.35	10	Ta	3255.69	18h
Pt I	4511.257	2	Ru	3256.331	50	Sc I	3255.678	15
Mn	4511.238	2	Re	3256.289	8	V I	3255.649	25

IRIDIUM (Ir)

Ionization Potential, 9.2 Volts

Most Sensitive Lines	Excitation Potential
3220.78 3133.321 2543.971	4.18 Volts

Ni I	3221.273	35
Yb	3221.22	2
W	3221.212	12d
Ru	3221.190	4
Ce II	3221.171	50
Ti I	3221.151	4
Cb	3221.125	4
Tm	3221.08	7
Ce	3221.061	2
Cb	3220.927	10
Ce	3220.871	30
Mo	3220.855	8
Rh	3220.78	4
Ir I	3220.780	100
Pt	3220.778	2
Er	3220.730	25
Hf II	3220.606	25
Pb	3220.538	50h
Nd	3220.529	2h
Cb	3220.488	3h
Dy	3220.46	10
Ce	3220.402	12s
Th	3220.304	12
Ti I	3220.277	3h

Gd	3133.859	25
W	3133.716	6
Ru	3133.697	12
Th	3133.619	10
Nd	3133.603	15
Ta	3133.553	15
Ce	3133.533	2
Hf II	3133.50	15
Zr II	3133.475	6
U	3133.424	8
Ce	3133.407	5
V II	3133.328	50
Ce	3133.327	20
Ir I	3133.321	40
Eu	3133.24	10
Zr I	3133.231	5
Fe	3133.226	5
Cd I	3133.167	200
Tb	3133.15	8
Ti I	3133.135	4
Hf II	3133.10	5
Sc II	3133.096	2
Gd	3133.092	3
Ir I	3133.086	20
Cb	3133.083	3
Dy	3132.98	6
Ru	3132.878	60

Ce	2544.376	2
U	2544.358	8
Ce	2544.269	3
Ta	2544.267	2
Co I	2544.253	50r
Rh	2544.223	8
Ru	2544.222	60
Re	2544.214	25
Au I	2544.19	30
W	2544.172	8
U	2544.042	4
Cb	2543.981	4
Ir I	2543.971	200h
Rh	2543.941	15
Fe	2543.920	40
Na I	2543.875	12R
Re	2543.831	20
Dy	2543.82	10
Na I	2543.817	6R
Os	2543.804	10
V I	2543.728	12
Gd	2543.71	2
Ru	2543.678	20
Re	2543.667	20r
Fe	2543.647	700
Zr II	2543.639	2
Mo	2543.611	3
Ce	2543.536	4
Mn	2543.452	4

IRON (Fe)

Ionization Potential, 7.83 Volts

Most Sensitive Lines	Excitation Potential
3719.935 I	3.32 Volts
3581.195 I	4.30 Volts
3020.64 I	4.09 Volts

Cb	3720.456	5
U	3720.394	6
Ti I	3720.384	40
Ce	3720.380	2
Tb	3720.36	8
Th	3720.309	15
Mo	3720.254	10
Pr	3720.222	15
Os I	3720.132	80
Th	3719.969	2
Ce	3719.946	2w
Fe I	3719.935	1000R
Ba I	3719.93	2
Ce II	3719.797	15s
Tm	3719.72	10
Mo	3719.692	3
U	3719.69	1h
Nd	3719.595	10
Mo	3718.553	5
Os I	3719.522	40
Gd	3719.464	40
Fe I	3581.649	4
W	3581.238	8
Fe I	3581.195	1000R
Mo	3581.00	2
Re I	3580.968	40w
Sc II	3580.927	12
U	3580.922	3
Sm	3580.906	40
Ta	3580.889	3
Ir I	3580.861	15
V I	3580.825	50
Ce	3580.779	10
Tb	3580.63	8
Gd	3580.629	5
Sm II	3580.586	2
Eu	3580.57	3
U	3021.22	10
Fe I	3021.073	700R
Ce	3021.038	15
U	3020.92	8d
Ce	3020.883	15
Ru I	3020.882	60
Mo	3020.693	5
Cr I	3020.673	200r
Cb	3020.666	5
Dy	3020.65	10
Fe I	3020.640	1000R
Co	3029.639	60
Tb	3020.58	3
U	3020.571	6
Hf	3020.529	15
Fe I	3020.489	300r
Zr II	3020.467	50
Tb	3020.29	8
U	3020.242	8
W	3020.214	7
Ca I	3020.15	2

LANTHANUM (La)*

Ionization Potential, 5.59 Volts

Most Sensitive Lines	Excitation Potential
4333.734 II	3.02 Volts
3949.106 II	3.53 Volts
3337.488 II	4.10 Volts

Ce	4334.227	3
Sm II	4334.149	200
V I	4334.092	20
Th	4333.942	5
Pr	4333.913	150
Eu	4333.749	6w
Er	4333.748	9
La II	4333.734	800
Dy	4333.72	2
Tb	4333.71	4
U	4333.524	5
Ce	4333.412	4
Nd	4333.394	5
Zr II	4333.262	8
Gd	4333.248	10
Nd	4333.217	3
Mo	4333.211	10
Pr	4333.148	40
Cr I	3949.585	5
U	3949.516	2
Tb	3949.509	10
Nd	3949.457	2
Cb	3949.455	1
Ag	3949.44	3
Pr	3949.438	150
Ru I	3949.417	10
Tb	3949.39	4
Ce II	3949.385	20
Cb	3949.328	3
U	3949.309	2
Tm	3949.27	50
Gd	3949.208	10
Fe	3949.15	4
Eu	3949.123	25w
Ce	3949.116	6
La II	3949.106	1000
U	3948.991	8
Th	3948.971	30
Ce	3948.949	4
Ca I	3948.901	40
Cr	3948.853	25
Fe	3948.779	150
Eu	3948.779	4
Ti I	3948.674	80h
Zr II	3337.924	2
Ce	3337.872	10
Th	3337.869	12
Ti II	3337.853	12
Yt I	3337.849	2
V	3337.846	2
Cu I	3337.844	70
Ru I	3337.823	60
Tm	3337.82	5
Ta	3337.799	100
Er	3337.79	20
U	3337.79	12
W	3337.682	10
Tb	3337.67	15
Fe	3337.666	125
Eu	3337.584	2h
W	3337.505	5
Ce	3337.502	20
bh Sr	3337.5	8
Ta	3337.498	35
Th	3337.488	3
La II	3337.488	800
U	3337.393	3
Re	3337.254	5d
Er	3337.25	15
Cr I	3337.22	10
Ho	3337.20	12
Co I	3337.172	60
Yb	3337.17	25
Th	3337.16	6
Sb	3337.15	2
Os	3337.138	2
Dy	3337.12	2
U	3337.036	10
Ni I	3337.014	6

*See list of sensitive rare earth lines at end of tables.

LEAD (Pb)

Ionization Potential, 7.38 Volts

Most Sensitive Lines	Excitation Potential
4057.820 I	4.36 Volts
3683.471 I	4.32 Volts
2833.069 I	4.4 Volts

Ce II	4058.244	18
Gd I	4058.231	100
Fe	4058.229	80
Pr	4058.19	6
Co I	4058.190	100
U	4058.16	10
Ti I	4058.144	50
Ta	4058.136	2
La II	4058.085	4
Tb	4058.02	2
bh Sr	4058.0	3
U	4057.955	1
Mn	4057.950	80
In	4057.866	80
V I	4057.825	10
Th	4057.823	2
Pb I	4057.820	2000R
Er	4057.819	30
Zn II	4057.71	80
Tb	4057.68	2
Sm	4057.653	10
Mg I	4057.632	10w
Ti I	4057.624	40
Mo	4057.584	10
Ce	4057.556	2
Ho	4057.55	2
W	4057.452	6
Mo	4057.438	4
Hf	4057.43	3
Dy	4057.40	4
Ni I	4057.347	2
Fe I	3684.112	300
Er	3684.014	6
Cb	3683.973	2h
Th	3683.944	3
W	3683.941	10
Eu	3683.85	8W
Pr	3683.846	4
Fe I	3683.616	3
Ru	3683.592	3
U	3683.59	2d
Ir	3683.523	5
Sb	3683.481	3
Mn	3683.474	12
Er	3683.472	25
Zn II	3683.471	20
Pb I	3683.471	300
Zr I	3683.470	2
Ag	3683.453	4
Ce	3683.393	2
W	3683.392	8
Th	3683.332	5
W	3683.310	8
Eu	3683.27	18w
Tb	3683.26	15
Tm	3683.20	10
Pr	3683.196	3
V I	3683.126	100
Fe I	3683.058	200
Ta	3683.058	18
Co I	3683.050	200R
Pt I	3682.983	8
Ta	2833.636	300w
W	2833.628	15
Ce	2833.580	2
Fe	2833.40	10
Th	3833.339	8
Ce	2833.309	50d
Cb	2833.304	1
Hf	2833.276	25
Eu	2833.25	10w
U	2833.244	8
Ir	2833.236	7
K	2833.14	2h
Pb I	2833.069	500R
Er	2833.061	25
Zr	2833.061	2
Eu	2833.056	3
Ce	2833.044	3
W	2832.952	10
Ce	2832.928	2
Ir	2832.774	5
Rh I	2832.769	5
Ce	2832.753	2
U	2832.645	2
Ru	2832.625	20
Ce	2832.568	2

LITHIUM (Li)

Ionization Potential, 5.37 Volts

Most Sensitive Lines	Excitation Potential
6707.844 I	1.84 Volts
6103.642 I	3.86 Volts
4602.863 I	4.52 Volts
3232.61 I	3.82 Volts

W	6708.18	20
V I	6708.17	2
Co	6707.857	200wh
Mo	6707.85	300w
Li I	6707.844	3000R
Ru	6707.524	5
Sm II	6707.45	50d
Sm	6707.1	2
Sm	6706.85	5
Nd	6104.106	3
Sm	6103.95	2
Sm	6103.723	4
Dy	6103.67	2
Li I	6103.642	2000R
Cb	6103.49	6
Sm	6103.374	30
Dy	6103.370	2
Fe I	6103.185	8h
Ce	6102.751	3

Tm	4603.42	35
Tm	4603.21	10
Sm	4603.116	5
Tb	4602.95	8
V I	4602.946	7
Fe I	4602.944	300
Gd	4602.944	10
Th	4602.884	5
Li I	4602.863	800
Cb	4602.860	2
Ru I	4602.808	15
Ce	4602.752	4
Hf	4602.713	6
bh La	4602.7	3
Eu	4602.63	15w
Lu	4602.60	3h
Zr I	4602.573	12
Pr	4602.562	10
Tb	4602.503	4
Nd	4602.242	10
Fe	3233.054	100
Ni I	3232.963	300R

Ce	3232.875	3
Co I	3232.874	60
Ti I	3232.791	8
Ru I	3232.751	50
Ce	3232.665	3
W	3232.652	9
Dy	3232.652	15
Sm	3232.620	10
Li I	3232.61	1000R
Os	3232.540	150
Rh I	3232.504	6
Sb I	3232.499	150
Sm	3232.497	4
W	3232.486	9
Pb	3232.353	30
Pd I	3232.32	2
Eu	3232.31	4w
Th	3232.308	8
Ce	3232.290	15
Ti II	3232.280	30
Ta	3232.279	25
W	3232.231	3
U	3232.157	12
W	3232.134	6

LUTECIUM (Lu)*

Ionization Potential, 5 Volts

Most Sensitive Lines	Excitation Potential
4518.57 I	
2911.39	
2615.42 II	

Pr	4519.115	3	Tb	2911.81	5	W	2911.001	10
bh Ca	4519.1	3	Mo	2911.765	5	Fe	2910.92	10
Hf	4519.031	1	U	2911.764	3			
Dy	4518.968	2	Cb	2911.745	8			
Os	4518.889	15	Sm	2911.712	6	Ce	2615.877	4
Ti I	4518.697	30	V	2911.655	1	Fe	2615.87	3
Pr	4518.687	2	U	2911.548	12	W	2615.695	1
Eu	4518.68	8w	Yb	2911.52	5	Re	2615.681	10
Mo	4518.668	4h	Ce	2911.514	8	Ta	2615.656	50
Th	4518.647	2	Er	2911.417	30	Ta	2615.465	50
Er	4518.640	40w				Ce	2615.453	5
Cr	4518.628	6	Lu	2911.39	100	W II	2615.445	6
U	4518.590	1	Os	2911.341	5	Fe	2615.422	25
Lu I	4518.57	300	Th	2911.324	8			
Dy	4518.538	6	U	2911.287	3	Lu II	2615.42	100
Mo	4518.440	5	Sm	2911.272	15			
Hf	4518.294	10	Re I	2911.231	8	Er	2615.420	15ℓ
Ce	4518.280	4	Cu I	2911.215	2h	Mo	2615.391	25
Tb	4518.208	2	Cr I	2911.145	40	Co I	2615.335	10
U	4518.078	1	Ce	2911.120	2	Yb	2615.26	3
Ti I	4518.032	100	U	2911.104	6	Ta	2615.250	40
			Fe	2911.08	3	W	2615.122	10
Mo	2911.915	30	Er	2911.069	4s	U	2615.120	2
Tm	2911.87	4	V II	2911.064	30	Ru	2615.093	60
			Fe	2911.01	3	Ir I	2614.984	25

*See list of sensitive rare earth lines at end of tables.

MAGNESIUM (Mg)

Ionization Potential, 7.61 Volts

Most Sensitive Lines	Excitation Potential
5183.618 I	5.09 Volts
3838.258 I	5.92 Volts
2852.129 I	4.3 Volts

Yb	5184.181	8
Ru	5184.034	4
Th	5183.986	6
W	5183.972	20
La I	5183.923	25
Pr	5183.848	5
Cb	5183.82	5h
Ti I	5183.72	8
Zr I	5183.705	6
Mg I	5183.618	500wh
Co	5183.610	35
Eu	5183.606	4
La II	5183.422	300
Cb	5183.33	5h
Ce	5183.197	10
Nd	5182.603	8
Ru	3838.728	10
Nd	3838.724	50
Dy	3838.67	10
Os I	3838.59	3
Ce	3838.542	35
W	3838.504	15
Hf II	3838.37	2
Eu	3838.36	2w
Pr	3838.341	5
Er	3838.339	10
Nd	3838.33	40
Ca	3838.318	2
Zr II	3838.283	10
Mg I	3838.258	300
Mn	3838.247	10
Eu	3838.24	4
Tm	3838.204	80
Li I	3838.15	5
U	3838.150	8
Ru I	3838.067	12
Fe	3838.036	1
Nd	3837.909	10
Mo	3837.882	3
Eu	3837.88	6w
Th	3837.880	10
Dy	3837.86	2
V	3837.852	5
Tb	3837.83	8
Na I	2852.828	100R
U	2852.750	15
Eu	2852.56	5W
V	2852.536	6
Ag	2852.53	1
Th	2852.502	2h
Ir	2852.479	2
U	2852.469	6
Re	2852.399	10
Ta	2852.355	5
Fe	2852.35	2
Ce	2852.237	3
Mo	2852.131	10h
Ir	2852.131	20
Fe	2852.13*	150
Mg I	2852.129	300R
Dy	2852.129	5
Ce	2852.124	50d
W	2852.10	1d
Hf II	2852.012	20
Cb	2851.977	4
Zr II	2851.967	12
Fe I	2851.798	200
V I	2851.748	30
Mg I	2851.65	25

*Under ordinary working conditions no iron line appears at λ2852.13 A.

MANGANESE (Mn)

Ionization Potential, 7.41 Volts

Most Sensitive Lines	Excitation Potential
4034.490 I	3.06 Volts
4033.073 I	3.06 Volts
4030.755 I	3.06 Volts
2576.104 II	4.8 Volts

Sm II	4035.101	50
Cb	4035.098	4
Pr	4035.07	2
Cr	4034.998	8
Ti I	4034.910	25
Th	4034.886	8
Co	4034.858	2
Tm	4034.74	10
Ce	4034.570	2
Cb	4034.523	10
Mn I	**4034.490**	**250r**
Gd	4034.38	5
Pr	4034.30	20
Ce	4034.259	2
Th	4034.256	10
Sc I	4034.23	8
Nd	4034.147	10d
Eu	4034.11	2
Zr II	4034.086	5
Cr I	4034.048	20
Nd	4034.012	4
U	4034.002	4
Mo	4033.999	3
Ti I	4033.906	40
Zr	4033.584	3
Sb	4033.543	70
Nd	4033.504	10
Gd	4033.491	10
U	4033.427	12
Ce	4033.378	2h
Re I	4033.307	40
Cr I	4033.263	30
Pr	4033.24	3
Cb	4033.203	5
Sr I	4033.191	6
Mn I	**4033.073**	**400r**
Cr	4033.072	15
Ta	4033.069	100
In	4033.066	4
Tb	4033.04	125
Ga I	4032.982	1000R
Sm	4032.977	20
Pr	4032.974	15
V I	4032.856	2
Dy	4032.847	8
Ce	4032.748	2
Tb	4032.705	3
Ti I	4032.632	35
Fe I	4032.630	80
V I	4031.219	10
Cr	4031.130	30
Th	4031.099	5
Pr	4031.09	12
Dy	4031.081	7
Ru I	4030.997	15
Mo	4030.915	3
Gd	4030.881	8
Th	4030.855	10
Ce	4030.853	2
Yt	4030.83	2
Zr I	4030.759	20
U	4030.758	5
Mn I	**4030.755**	**500r**
Cr	4030.681	40
Ta	4030.668	10
Eu	4030.66	5w
Sc I	4030.657	10
Ti I	4030.514	80
Fe I	4030.492	120
Nd	4030.470	20
Sm II	4030.425	10
Sr I	4030.377	40
Ce II	4030.344	18
Ca	4030.3	10
Th	4030.293	8
Eu	4030.203	10w
Cb	2576.597	3
Mo	2576.563	2
V	2576.480	1
W II	2576.360	2
Th	2576.336	6
Re	2576.319	15
Hg I	2576.295	20
Rh	2576.229	2
W	2576.165	2
Zr I	2576.105	8
Mn II	**2576.104**	**300R**
Co	2576.104	30
Cb	2575.963	1
Ce	2575.933	6
W	2575.897	9
Rh I	2575.75	2
Ag	2575.744	10h
Fe	2575.744	80
Ir I	2575.743	10
Mn	2575.509	150

MERCURY (Hg)

Ionization Potential, 10.38 Volts

Most Sensitive Lines	Excitation Potential
4358.35 I	7.7 Volts
2536.519 I	4.9 Volts

Th	4358.832	3
Tb	4358.77	2
Zr I	4358.742	10
Ho	4358.74	3
Yt II	4358.726	60
Nd	4358.699	15
Re I	4358.688	80
U	4358.654	2
Ta	4358.654	10
Sc I	4358.645	10
Pd I	4358.599	25
Th	4358.556	4
Mo	4358.551	20w
Fe I	4358.505	70
Dy	4358.461	25
Tb	4358.43	3
Hg I	4358.35	3000w
Pt I	4358.336	2
Th	4358.333	3
Ir	4358.279	8
Er	4358.172	4
Nd	4358.169	50
Os	4358.141	9
Ta	4358.033	3
Os	4357.980	12
Re	4357.97	15
La I	4357.917	5
Ce	4357.907	12

Rh	2537.039	15
Lu	2536.95	10
V	2536.926	10
Mo	2536.849	25
Fe II	2536.817	10
U	2536.794	4
Tb	2536.75	3
Rh	2536.706	15
Fe II	2536.673	1
Ta	2536.67	2h
Ir	2536.665	3
W	2536.605	1
U	2536.600	3
Bi	2536.56	5h
Th	2536.558	5
Hg I	2536.519	2000R
Co I	2536.493	1
Pt I	2536.487	100
U	2536.238	4
Ta	2536.227	100W
Fe	2536.224	3
Ru	2536.216	12
Ir	2536.127	2
W	2535.988	4

MOLYBDENUM (Mo)

Ionization Potential, 7.35 Volts

Most Sensitive Lines	Excitation Potential
3902.963 I	3.16 Volts
3798.252 I	3.25 Volts
3170.347 I	3.89 Volts

Nd	3903.510	10
Sm	3903.412	60
Ce	3903.342	15
Dy	3903.332	8
W	3903.298	6
U	3903.262	10
V II	3903.262	3
Eu	3903.240	10W
Cr I	3903.164	35
Ce	3903.120	2
Tb	3903.11	3
Th	3903.093	15
Mo I	**3902.963**	**1000R**
Fe I	3902.948	500
Cr I	3902.915	100
Ce	3902.89	8
Ir I	3902.849	8
Re	3902.821	3
Ru	3902.816	5
Er	3902.766	10
Ce	3902.745	2
Gd I	3902.717	25
W	3902.684	5
Ir I	3902.662	8
Re	3902.583	6
La I	3902.576	20
U	3902.561	18
V I	3902.558	6
Ce	3902.509	3
Ir I	3902.506	10
Pr	3902.470	60
Tm	3798.76	20
Eu	3798.71	2wh
Ir I	3798.666	5
Hf	3798.662	5
V I	3798.661	7
Dy	3798.65	2
Er	3798.65	4
Ce	3798.624	3
Tb	3798.59	15
Tm	3798.55	15
FeI	3798.513	400
Ce	3798.51	3
Yb	3798.44	4
Ti I	3798.314	10
Ir	3798.272	8
Er	3798.25	5
U	3798.259	2
Mo I	**3798.252**	**1000R**
Ce	3798.238	2
Yb	3798.17	4
Cb	3798.121	50
Th	3798.103	5
Ce	3798.08	2
Ir	3798.059	6
RuI	3798.052	30
Fe I	3797.949	4
Tb	3797.93	15
Ir	3797.924	2
Hf II	3797.923	25
Th	3797.91	2
Nd	3797.89	20d
U	3797.773	10
U	3170.855	10
Dy	3170.746	10
Ni I	3170.715	4
Ag	3170.579	5
U	3170.538	3
Ce	3170.528	2
Th	3170.429	10
Eu	3170.38	15
Mo	**3170.347**	**1000R**
Fe II	3170.346	10
Ta	3170.289	250w
Sm II	3170.203	15
W	3170.201	15
Cb	3170.160	2
Ru	3170.093	30
U	3170.09	2
Ce	3170.069	12
Nd	3170.015	10
U	3169.989	6
Dy	3169.978	100
W	3169.928	10
Tm	3169.89	15
Sm II	3169.870	25
Ca I	3169.854	10

NEODYMIUM (Nd)*

Ionization Potential, Volts

Most Sensitive Lines	Excitation Potential
4303.573 II	2.87 Volts
4247.367 II	2.91 Volts
4012.250 II	3.70 Volts

Tb	4304.02	12	U	4247.136	10
Mo	4304.020	12	Eu	4247.069	15
Ti	4303.961	8	Ce	4246.938	3
Cb	4303.881	3	P	4246.88	70
Er	4303.813	12	Nd	4246.879	10
Dy	4303.60	3			
Hf	4303.596	10			
Pr	4303.594	100	Nd	4012.704	15
Nd II	4303.573	100	Er	4012.58	4
			Dy	4012.523	4
Ta	4303.54	1	Mo	4012.51	3
W	4303.533	4	Th	4012.497	15
V	4303.527	15	Cr	4012.469	70
Gd	4303.456	6	Tb	4012.45	5
U	4303.325	6	Ti II	4012.391	35
Co I	4303.236	15	Ce I,II	4012.388	60
Fe II	4303.168	12	Mo	4012.270	3
Pr	4303.139	20	Re	4012.260	25
			Er	4012.253	12
Eu	4247.831	5h	Zr I	4012.252	20
Ev	4247.73	8			
Ce	4247.695	2	Nd II	4012.250	80
Re	4247.694	3			
Cb	4247.690	2	U	4012.161	6
Pr	4247.662	60	Co I	4012.160	2
Ce	4247.653	2	Ce	4012.139	40
Th	4247.599	8	Ta	4012.111	5h
Fe I	4247.433	200	Mo	4011.966	25
U	4247.430	5	Hf	4011.944	3
Sm II	4247.395	15	Mn	4011.905	12
Nd II	4247.367	50			
Dy	4247.36	30			

*See list of sensitive rare earth lines at end of tables.

NICKEL (Ni)

Ionization Potential, 7.606 Volts

Most Sensitive Lines	Excitation Potential
3524.541 I	3.53 Volts
3492.956 I	3.64 Volts
3414.765 I	3.64 Volts

Sm	3525.065	2
Ba I	3524.985	20
Mo	3524.981	5
Cb	3524.936	2
Dy	3524.92	6
Er	3524.920	20
Ru I	3524.902	12
V II	3524.715	10
W	3524.681	7
Mo	3524.646	5
Dy	3524.61	6
Ni I	3524.541	1000R
Mn	3524.540	15
Sm	3524.538	10
Zr I	3524.538	9
Pr	3524.47	3
Ir	3524.372	2h
Eu	3524.34	3w
W	3524.246	9
Zr	3524.242	12
Fe I	3524.241	60
Ti	3524.240	2
Cu I	3524.239	40
Mo	3524.228	8
Gd	3524.198	25
Ru	3524.152	6
Ce	3524.073	8
Fe	3524.071	50
Fe II	3493.474	40
Cb	3493.473	3
Ta	3493.465	15W
Sm II	3493.408	2
Eu	3493.407	7
U	3493.407	2
Mo	3493.337	6
U	3493.333	6
Fe I	3493.290	1
Ti I	3493.280	15
Tb	3493.27	8
Dy	3493.26	3
Ru	3493.220	20
W	3493.195	6
V II	3493.167	15
Pr	3493.158	10
Ce	3493.110	12
Ho	3493.10	10
W	3493.036	5
Tb	3492.99	15
Ce	3492.983	3
Eu	3492.969	2
Tb	3492.96	15
Mn	3492.960	10
Ni I	3492.956	1000R
Sm	3492.895	3
Mo	3492.825	3
U	3492.799	2
Sm	3492.775	3
Pr	3492.73	4
Th	3492.683	2
Sm II	3492.622	8
Tm	3492.59	20
Tb	3492.56	15
Ce	3492.559	3
Er	3492.543	25d
Dy	3492.52	2
Ce	3492.486	5
Ir	3415.241	10
Os	3415.224	5
Th	3415.13	2
Tb	3415.12	8
Pr	3415.079	4
Ce	3415.069	8
Sm II	3414.953	10
Zr I	3414.950	2
Ho	3414.92	30
Dy	3414.830	35
Er	3414.79	8
Eu	3414.773	40
Pr	3414.767	7
Ce	3414.766	5
Ni I	3414.765	1000R
Co I	3414.736	200W
Zr II	3414.661	20
Ru I	3414.642	50
U	3414.63	3d
Ce	3414.605	5
Ag I	3414.55	4
Th	3414.513	6
Yt	3414.49	3
U	3414.36	8d
Ce	3414.313	8
Cr	3414.305	8wh
Dy	3414.30	2
Nd	3414.298	10
Ru	3414.282	12

NIOBIUM (Cb)

Ionization Potential, Volts

Most Sensitive Lines	Excitation Potential
4079.729 I	3.11 Volts
4058.938 I	3.17 Volts

Fe I	4080.221	60
Cr	4080.221	15
bh Sr	4080.1	2
Ce	4080.025	5
Ir	4079.897	25
U	4079.847	1
Fe I	4079.845	80
Sm	4079.829	20
Pr	4079.786	50
W	4079.785	4
Cb I	4079.729	500w
Ti I	4079.721	40
Ce	4079.667	15
Th	4079.612	5
Dy	4079.595	8
Mn	4079.422	50
Re	4079.363	20
Mo	4079.342	4
Ru I	4079.277	12

Mn	4059.392	20
Eu	4059.376	25
Pr	4059.37	4
Ce	4059.367	3
Gd	4059.346	10w
Ce II	4059.322	8h
Th	4059.259	8
W	4059.254	5
Ir	4059.234	30
Eu	4059.035	4
U	4059.025	1
Zr I	4058.985	8
Mg	4058.96	2
Cb I	4058.938	1000w
Mn	4058.930	80
Ca I	4058.930	3d
Tm	4058.92	20
Ru	4058.882	10
Sm II	4058.867	30
Tb	4058.81	3W
Pr	4058.778	25
Cr	4058.772	80
Fe I	4058.760	40
Zr I	4058.624	9
Co I	4058.600	100
Ta	4058.464	10

OSMIUM (Os)

Ionization Potential, 8.7 Volts

Most Sensitive Lines	Excitation Potential
3058.66 I	4.03 Volts
2909.061 I	4.2 Volts

Ru	3059.169	50	Dy	2909.325	2
Fe I	3059.086	600r	Fe	2909.31	4
Eu	3059.00	20	U	2909.250	6
Tm	3058.99	10	Ru	2909.224	12
U	3058.98	8d	Yb	2909.19	2
Ru I	3058.786	30	W	2909.123	8
Re I	3058.786	50	Mo II	2909.116	25
Os I	3058.66	500R	Os I	2909.061	500R
Ru I	3058.655	30	Cr I	2909.052	60r
Ir	3058.653	5	Eu	2909.01	40
Ta	3058.636	50	Cb	2908.979	1
Mo	3058.597	20	Ta	2908.910	150
Ce	3058.551	12	Cb	2908.881	2
Fe	3058.493	3	Mn	2908.879	10
Th	3058.431	10	U	2908.878	2
Th	3058.142	8	Fe	2908.859	80
			Hf II	2908.858	3
Ir	2909.558	18	V II	2908.817	70r
Fe	2909.503	70	Cd I	2908.74	5ℓ
Yb	2909.48	2	Tm	2908.69	5
Ho	2909.42	40	Er	2908.535	6

PALLADIUM (Pd)

Ionization Potential, 8.3 Volts

Most Sensitive Lines	Excitation Potential
3421.24 I	4.62 Volts
3404.580 I	4.44 Volts

Cr	3421.72	12
Ce	3421.714	3
U	3421.69	8
Os	3421.687	30
Eu	3421.667	5
Cr	3421.64	2h
Ho	3421.64	20
Co I	3421.626	20
Re	3421.579	15
Ce II	3421.542	5
Ba I	3421.48	2
Hf II	3421.45	3
Zr I	3421.419	3
U	3421.38	8d
Co I	3421.348	3
Ni I	3421.342	30
Dy	3421.32	7
Sm	3421.297	2
Mo	3421.250	6
Pd I	3421.24	2000R
Cr II	3421.212	50
Ta	3421.212	1
Ni I	3421.204	4
Th	3421.189	10
Cb	3421.162	10w
W	3421.134	3d
Pr	3421.112	10
Ce	3421.071	6
Er	3421.065	9
Ba I	3421.01	3
Ce	3420.955	5
Dy	3420.81	5
Mn	3420.795	8
Co I	3420.792	80
Re I	3420.758	40
Ni I	3420.741	30
Ti I	3405.094	20
Ag	3405.03	3
Dy	3404.99	4
V I	3404.960	8
U	3404.933	3
Ce	3404.910	18
Mo	3404.864	6
Zr II	3404.832	40
W	3404.803	8
Sm	3404.767	2
Nd	3404.763	4
Fe I	3404.754	2
Re I	3404.724	100
Tb	3404.71	3
Th	3404.654	4
Pd I	3404.580	2000R
La I	3404.52	9
Ce	3404.428	12
Fe I	3404.359	100
Mo	3404.342	20
Fe I	3404.304	25
Tb	3404.24	15
W	3404.224	8
Ta	3404.163	5
Er	3404.13	8

PHOSPHORUS (P)

Ionization Potential, 11.1 Volts

Most Sensitive Lines	Excitation Potential
2554.93 I	7.1 Volts
2553.28 I	7.1 Volts
2535.65 I	7.2 Volts
2534.01 I	7.2 Volts

Fe II	2555.442	2
Mo	2555.42	3
Rh I	2555.360	100
Ir I	2555.347	25
Cb	2555.319	1
Os	2555.273	10
Fe	2555.220	10
U	2555.210	4
W	2555.205	10
W II	2555.091	10
Fe II	2555.066	20
Ta	2555.052	50
Re	2554.931	15
P I	**2554.93**	**60**
Ta	2554.907	50h
W II	2554.862	15
V I	2554.862	15
Cb	2554.795	1
Eu	2554.785	10
Ru	2554.687	8
W	2554.668	4
Re	2554.631	5
Ta	2554.622	50
Mg I	2554.62	4
Sb	2554.617	30
Fe	2554.520	2
Cd I	2554.51	3
Os	2554.465	20
Ir I	2554.399	15
U	2553.73	3
Mo	2553.698	15
V	2553.669	10
W	2553.598	10
Ce	2553.588	2
Cd I	2553.56	25
Re	2553.556	5
Fe	2553.50	2
Cb	2553.492	1
Ce	2553.456	2
Ag II	2553.407	2
Ni I	2553.377	20
Co I	2553.374	10r
Ce	2553.344	3
Ru	2553.310	6
P I	**2553.28**	**80**
Fe	2553.185	10
Ta	2553.181	10h
W	2553.162	12
Cr I	2553.062	20
Zr II	2553.047	2
V	2553.024	7
Co I	2553.003	40r
Ti	2552.98	10R
V	2552.962	10
Mo	2552.873	20
Fe I	2552.832	5
Fe	2552.773	20
Ir	2536.127	2
W	2535.988	4
Ni	2535.967	25
Pt	2535.967	25
Co I	2535.964	10r
Ta	2535.96	4
U	2535.90	5
Ti II	2535.871	20
Th	2535.870	5
P I	**2535.65**	**100**
Fe I	2535.604	1000
Ta	2535.598	50h
Fe	2535.364	1
W	2535.332	8
Ag II	2535.307	10
Zr II	2535.15	1
Cb	2534.441	1
Fe II	2534.416	7
Cr II	2534.336	8
V I	2534.259	2
Ce	2534.180	2
Os	2534.166	8
Ta	2534.162	3
W	2534.146	2
Re	2534.101	10
Rh	2534.072	4
P I	**2534.01**	**50**
Ir I	2534.006	2
Ru	2534.001	4
W	2533.982	10
V	2533.963	1
Cb	2533.920	1
Cd I	2533.91	2
Co	2533.81	5r
V	2533.805	10
U	2533.804	4
Fe	2533.803	12
W	2533.633	10
Fe II	2533.627	8
Rh	2533.591	2

PLATINUM (Pt)

Ionization Potential, 8.9 Volts

Most Sensitive Lines	Excitation Potential
3064.712 I	4.03 Volts
2659.454 I	4.6 Volts

U	3065.198	6	Al	3064.304	20
Dy	3065.14	4	Mo	3064.279	80
Sc II	3065.106	12d	Fe	3064.217	4
Cr	3065.067	20			
Yb	3065.048	4	Ir I	2659.946	2
Mo	3065.042	30	Ga	2659.866	5
Sm	3065.008	4	Th	2659.86	3
Er	3064.97	3	Os	2659.833	30
W	3064.937	10s	Re	2659.792	15
Yb	3064.91	2	Ce	2659.716	2
U	3064.908	1	Ta	2659.655	15
Er	3064.84	7	Ru I	2659.615	80
Ru	3064.838	70	V	2659.606	9
Ir I	3064.790	5	bh C	2659.6	20
			Rh I	2659.472	3
Pt I	3064.712	2000R	Pt I	2659.454	2000R
Hf II	3064.68	10	Eu	2659.42	4
Zr II	3064.634	5	Ta	2659.41	20
Ni I	3064.623	200r	Yb	2659.28	2
Re	3064.600	20	Fe	2659.24	8
U	3064.591	4	Ir	2659.144	4
Mo	3064.555	15	Cb	2659.052	3h
Cb	3064.533	5w	U	2659.025	8
Ir I	3064.509	20	Re	2659.023	25
Na II	3064.372	2	Rh I	2659.011	2
Co I	3064.370	100			

POTASSIUM (K)

Ionization Potential, 4.32 Volts

Most Sensitive Lines	Excitation Potential
7698.979 I	1.60 Volts
7664.907 I	1.61 Volts
4047.201 I	3.05 Volts
4044.140 I	3.05 Volts

Yb	7699.49	2000
Ta	7699.14	5
K I	7698.979	5000R
Nd	7698.94	2h
Yt	7698.00	4
Sc I	7697.73	20
Dy	7666.78	2
bh Ti	7666.4	6
Sc I	7665.72	5
K I	7664.907	9000R
Cu II	7664.70	5
La I	7664.34	8
Fe I	7664.302	15
Yt I	4047.632	50
Ce	4047.620	3
U	4047.610	18
Mo	4047.563	4
Ho	4047.50	3
Mo	4047.398	4
Ce	4047.392	4
Sm II	4047.363	8
Ca	4047.351	2
Ir	4047.329	4
Fe I	4047.310	3
Ce	4047.275	18
Mo	4047.204	4
K I	4047.201	400
Tb	4047.16	9
Nd	4047.158	12
Pr	4047.098	20
Gd	4047.093	6
U	4047.05	6
Er	4046.960	8
Mo	4046.886	3
Ce	4046.853	3
Gd	4046.842	10
Ni I	4046.761	2
Cr I	4046.760	30
Fe I	4044.611	70
Zr I	4044.564	25
Tm	4044.47	15
Ca	4044.419	5d
U	4044.416	18
Hf	4044.39	10
Nd	4044.347	3
Ce	4044.330	4h
W	4044.288	15
K I	4044.140	800
Sm	4044.113	4
Cb	4044.105	5
Hg II	4044.10	5
Ce	4044.062	3
U	4044.041	1
Gd	4044.030	3h
Eu	4043.97	20
Ce	4043.955	3
Fe I	4043.905	25
Sc I	4043.804	12
Ti I	4043.775	20
Ce	4043.747	3
Mo	4043.738	8
Gd	4043.710	5
Cr	4043.696	30

PRASEODYMIUM (Pr)

Ionization Potential, Volts

Most Sensitive Lines	Excitation Potential
4225.327 II	2.92 Volts
4222.98 II	2.98 Volts
4179.422 II	3.16 Volts

Gd	4225.853	150	Cr I	4223.470	15	Ti I	4179.885	4
U	4225.75	1	Dy	4223.38	2	Zr II	4179.809	15
Ce	4225.746	5	Tb	4223.32	10	Ce	4179.806	1
Sc I	4225.58	4	U	4223.30	1h	Tb	4179.80	6
Nd	4225.556	3	Nd	4223.208	15	Cb	4179.755	10
Ir	4225.496	15	Ir	4223.159	15	Re	4179.75	2h
Fe I	4225.465	80	Ce	4223.153	3	Th	4179.718	8
Zr I	4225.463	6	Lu	4223.09	1	U	4179.634	2
U	4225.369	8	Sm	4223.056	3	Nd	4179.585	10
Pr II	4225.327	50	Gd	4222.98	10	Hf II	4179.53	5
Sm II	4225.318	40	Pr II	4222.98	125	Cu II	4179.508	1h
Gd	4225.264	3	Mo	4222.961	15	Dy	4179.46	3
Zr I	4225.263	4	U	4222.94	1	U	4179.432	10
Mo	4225.248	5	Tb	4222.91	6W	Pr II	4179.422	200
V II	4225.225	3	Ce	4222.884	3	V I	4179.419	20
Dy	4225.153	40	Na I	4222.8	3	Er	4179.401	5
Gd	4225.148	20	U	4222.739	6	Eu	4179.40	2
Ho	4225.13	3	Cr I	4222.732	100	Ba	4179.372	6
Co	4225.109	5	Tb	4222.71	9	Ce II	4179.289	10
Ru	4225.092	25	Tm	4222.67	10	Cr	4179.257	100
Gd I	4225.028	15	Ce	4222.599	80	Co I	4179.229	15
Mo	4224.929	5	Mo	4222.411	20	Ce	4179.079	8
Eu	4224.88	4				U	4179.001	15
Tb	4224.85	5				Tb	4178.97	50d
Nd	4224.847	15				Fe II	4178.868	10
Ti I	4224.793	40						

RHENIUM (Re)

Ionization Potential, 7.85 Volts

Most Sensitive Lines	Excitation Potential
4889.17 I	2.52 Volts
3460.47 I	3.57 Volts

Pr	4889.663	5	Sc I	3460.700	6
Ce	4889.587	20	Pr	3460.663	3
Cb	4889.557	3	Dy	3460.64	4
Dy	4889.325	5	Sm	3460.63	3w
Mo	4889.216	25	Ce	3460.581	2
Gd	4889.203	60	Nd	3460.581	25
			Ir	3460.544	3
Re I	4889.17	2000w	Re I	3460.47	1000W
Nd	4889.106	8			
Fe I	4889.009	2wh	Cr I	3460.430	40
Er	4888.874	3	Dy	3460.40	20
Fe I	4888.651	2	Tb	3460.38	15
Ru	4888.607	6	U	3460.351	3
Cr I	4888.530	100	Mn II	3460.328	60
			La II	3460.31	2
			Eu	3460.290	15
Er	3460.968	20ℓ	Yb	3460.27	30
Ho	3460.95	6	Mo	3460.226	5
W	3460.784	3	Ce	3460.163	6
Mo	3460.784	25	Nd	3460.13	6
Ce	3460.783	2	U	3460.058	5
U	3460.781	2	Dy	3460.05	5
Pd I	3460.774	300r	Mn II	3460.018	5
Co I	3460.719	18	Zr II	3459.933	20

RHODIUM (Rh)

Ionization Potential, 7.7 Volts

Most Sensitive Lines	Excitation Potential
3692.357 I	3.34 Volts
3434.893 I	3.59 Volts

Mn	3692.812	50
Nd	3692.768	12
Sm	3692.763	20
U	3692.750	10
W	3692.725	7
Ir I	3692.694	15
Eu	3692.66	5w
Er	3692.652	20
Fe	3692.652	5
Ho	3692.65	10
Mo	3692.645	3
Zr II	3692.635	2
Th	3692.571	10
Ce	3692.552	2
Yt I	3692.529	7
Ru	3692.370	6
Rh I	**3692.357**	**500hd**
Pr	3692.293	4
V I	3692.225	200R
Ce	3692.222	3
Sm II	3692.221	90
Eu	3692.22	4wh
Ir	3692.20	2
Ti	3692.134	12
Re	3692.126	15
Mo	3692.081	5
Th	3692.080	8
U	3692.052	4
Tb	3692.02	15
Eu	3691.98	3W
U	3691.917	6
Th	3691.881	8

Ti	3435.432	10
Dy	3435.27	4
Sm II	3435.256	5
Os	3435.256	20
W	3435.243	6
Ce	3435.207	20
Eu	3435.205	35
U	3435.200	10
Ru I	3435.186	60
Eu	3435.064	12
Tb	3434.92	30
Rh	**3434.893**	**1000r**
Hf	3434.89	5
Os	3434.889	20
U	3434.805	2h
Mo	3434.790	50
Th	3434.762	8
Ir I	3434.757	10
Pr	3434.757	20
Eu	3434.74	3
Ag I	3434.646	2h
Er	3434.634	12
U	3434.614	12
Yb	3434.61	5
Tb	3434.54	15
Ta	3434.500	35
Mo	3434.496	5
Pr	3434.486	3
Dy	3434.373	80

RUBIDIUM (Rb)

Ionization Potential, 4.16 Volts

Most Sensitive Lines	Excitation Potential
7947.60 I	1.55 Volts
7800.227 I	1.58 Volts
4215.556 I	2.93 Volts
4201.851 I	2.94 Volts

Ru I	7948.15	15
Sm II	7948.12	100d
Mn	7948.10	2
Rb I	**7947.60**	**5000R**
V I	7947.38	8
Sm II	7947.00	15d
Si	7801.30	3h
Re	7801.05	4
Zr I	7800.74	2
Sc I	7800.44	40
Rb I	**7800.227**	**9000R**
Si	7800.0	4Wh
Re	7799.58	3
Zr I	7799.51	2
Ta	7799.51	3
Zn I	7799.365	10
U	4215.99	5
Pr	4215.98	4
Fe I	4215.970	2
Er	4215.964	9
Tb	4215.95	3
Rb I	**4215.556**	**1000R**
Tm	4215.53	10
Sr II	4215.524	300r
U	4215.51	3
Re	4215.506	20
Fe I	4215.425	60
Na I	4215.4	3
W	4215.382	12
Zr I	4215.313	4
Dy	4215.169	50
Os	4215.155	8
Pr	4215.14	8
Tb	4215.13	30d
Gd	4215.024	200
V II	4202.34	6
Dy	4202.250	20
Mo	4202.219	5
Ni I	4202.154	5
Os	4202.062	100
Fe I	4202.031	400
Eu	4202.03	5
Ta	4201.97	5h
Th	4201.852	8
Rb I	**4201.851**	**2000R**
Mn	4201.757	40
Ni I	4201.723	30
U	4201.628	1
Er	4201.60	8d
Pr	4201.529	30w
Cb	4201.519	10
La	4201.50	2
Zr I	4201.457	50
Os	4201.449	30
U	4201.416	8
Dy	4201.372	8

RUTHENIUM (Ru)

Ionization Potential, Volts

Most Sensitive Lines	Excitation Potential
3498.942 I	3.53 Volts
3436.737 I	3.74 Volts

Ce	3499.466	2	Th	3498.625	6
Ce	3499.388	4	U	3498.600	2
Ir I	3499.368	2	Ce	3498.562	8
Tb	3499.34	15	Os	3498.536	80
U	3499.327	6	Cb	3498.434	2
Ce	3499.300	4			
Os	3499.266	3	Ni I	3437.280	600R
Mo	3499.199	3	W II	3437.220	3
Ir I	3499.112	5	Mo	3437.216	25
Er	3499.104	18	Zr II	3437.137	15
Ti I	3499.099	25	Sm II	3437.115	15
Pr	3499.088	40	U	3437.09	3d
Ho	3499.08	10	Ta	3437.074	2r
U	3499.071	6	Fe	3437.051	80
Th	3498.986	8	Th	3437.027	5
Hf	3498.985	6	Ir I	3437.015	20
Ir	3498.951	25	Tb	3436.97	15
Yt I	3498.943	8	Cb	3436.962	20r
Ru I	3498.942	500R	Co I	3436.960	10
			Ce	3436.959	5
Dy	3498.939	15	Dy	3436.95	3
Ce	3498.924	2	Cb	3436.830	2
Mo	3498.923	3	U	3436.780	12
Sc I	3498.912	8	Ru I	3436.737	300R
Ho	3498.87	8			
Ce	3498.826	2	Ce	3436.727	3
Fe	3498.758	1h	Sm	3436.70	3
Ir	3498.737	15	Th	3436.687	3d
Tb	3498.73	8	Pr	3436.629	15
Rh I	3498.730	500	Cu I	3436.543	7
Er	3498.711	10	Yb	3436.46	5
Ce	3498.679	15	Er	3436.336	10
Dy	3498.67	50	Ru I	3436.332	12
Cb	3498.629	30	Ce	3436.304	15

SAMARIUM (Sm)*

Ionization Potential, 5.6 Volts ?

Most Sensitive Lines	Excitation Potential
4424.342 II	3.27 Volts
4296.75 I	3.37 Volts
3568.258 II	3.94 Volts

W	4424.906	8	Cr I	4297.050	100	Dy	3568.65	4
Ru	4424.781	25	Ir	4297.030	3	Os	3568.566	2
Ir	4424.752	3	Ni I	4296.984	2	U	3568.525	2
Pr	4424.595	90	Gd	4296.90	4	Ce	3568.513	2
Er	4424.570	10	Sr	4296.82	3	Tb	3568.51	50
V I	4424.563	20	Ce	4296.786	5	Cb	3568.506	10
Ce	4424.540	3	Rh I	4296.770	40	Ag	3568.435	2
Tb	4424.46	3	Er	4296.752	10d	Co I	3568.426	2
Ti I	4424.393	15	Sm I	4296.750	100	Fe I	3568.423	20
Nd	4424.343	50	Zr II	4296.742	3	Cr	3568.418	6wh
Sm II	4424.342	300	Ru	4296.689	7	W	3568.418	4
Ce	4424.314	6	Ce	4296.680	40	Dy	3568.33	4
Cr I	4424.281	25	Cr	4296.631	15	Pr	3568.29	5
Mo	4424.197	5	Mo	4296.624	15	Sm II	3568.258	40
Ce	4424.140	3	Fe II	4296.585	2	Re	3568.231	40
Gd	4424.102	25	Pr	4296.55	15	Mo	3568.181	3
Cr	4424.075	10	Hf	4296.41	10	Zr II	3568.135	4
Rh I	4424.047	5	Ce	4296.371	10	Ce	3568.126	10
Th	4423.945	8w	Nd	4296.363	12	Mo	3568.067	3
Pr	4423.933	5	Tb	4296.35	20	W	3568.040	10
V I	4423.914	7	Dy	4296.34	2	Sb II	3568.00	1
			Gd	4296.291	40	Ir	3567.995	15
Er	4297.30	2	Cr	4296.275	15	Cb	3567.995	2
Ca	4297.26	2h				Th	3567.978	5
Gd	4297.179	100	Cb	3568.725	5	Tb	3567.86	8
U	4297.112	18	U	3568.690	3	Lu	3567.84	100
			Tm	3568.68	5	Mo	3567.735	2

*See list of sensitive rare earth lines at end of tables.

SCANDIUM (Sc)

Ionization Potential, 6.7 Volts

Most Sensitive Lines	Excitation Potential
4246.829 II	3.22 Volts
4023.688 I	3.09 Volts
3911.810 I	3.18 Volts

Fe I	4247.433	200
U	4247.430	5
Sm II	4247.395	15
Nd	4247.367	50
Dy	4247.36	30
U	4247.136	10
Eu	4247.069	15
Ce	4246.938	3
P	4246.88	70
Nd	4246.879	10
Sc II	**4246.829**	**80**
Re	4246.813	25
Ru	4246.734	20
Ce	4246.711	30
Tb	4246.59	12
Gd	4246.547	150
Ce	4246.398	10
Tm	4246.38	20
Th	4246.338	3
Ru	4246.334	15
Cb	4246.295	8
U	4246.261	30
Ru	4024.305	7
Tm	4024.24	7
Fe I	4024.104	8
Mo	4024.091	30
Tb	4024.07	40W
Pr	4024.07	5
Zr I	4023.981	30
Ho	4023.93	4
Eu	4023.84	2
Ru I	4023.833	25
Nd	4023.824	12
Gd	4023.74	3h
Cr	4023.739	40
Pr	4023.737	3
Dy	4023.722	10
Tb	4023.716	6
Sc I	**4023.688**	**100**
Ce	4023.640	4
U	4023.597	3h
La II	4023.588	50
Th	4023.533	3
Cr I	4023.43	15
Co I	4023.403	200
V II	4023.389	10
Ce	4023.370	8
Re I	4023.353	40w
Gd I	4023.350	20
Zr I	4023.302	5
Sc I	4023.223	60
Sm II	4023.223	30
U	3912.234	2
Nd	3912.228	20
V I	3912.207	50
Ce II	3912.189	25
Ta	3912.127	10
Ru	3912.112	10
Fe	3912.05	5wh
Cr	3911.999	40wh
Pr	3911.989	20d
Eu	3911.97	4w
Mo	3911.945	5
Th	3911.914	8
Er	3911.911	5
Nd	3911.909	12
Cr I	3911.82	10
Os	3911.812	30
Sc I	**3911.810**	**150**
Ho	3911.80	3
Pr	3911.798	8
Re	3911.775	3
Lu	3911.77	3h
Ce	3911.726	3
Fe	3911.699	1
Dy	3911.677	5
U	3911.673	18
Gd	3911.66	5
Eu	3911.606	5
Er	3911.558	8
Mn	3911.419	15
Ti I	3911.362	7
Th	3911.308	5
Pr	3911.307	5

SILICON (Si)

Ionization Potential, 8.12 Volts

Most Sensitive Lines	Excitation Potential
2881.578 I	5.1 Volts
2516.123 I	4.9 Volts

Th	2882.014	10	W	2516.577	12
Ti I	2881.951	2	Fe I	2516.570	10
Cr	2881.931	1	Yb	2516.362	2
U	2881.909	4	Fe I	2516.250	2
Ce	2881.772	2	Si I	2516.123	500
Ir	2881.737	3	V	2516.118	25
Ir I	2881.643	7	Re	2516.116	125
Dy	2881.59	2h	Ta	2516.111	6
Co	2881.580	4	Dy	2516.11	5
Si I	2881.578	500	Mo	2516.109	25
Ce	2881.578	40	Ru	2516.006	20
Gd	2881.578	40	Zn I	2515.807	150w
Ce	2881.420	4s	W II	2515.798	1
Ir	2881.357	4	Ru	2515.759	6
Gd	2881.328	2	Rh I	2515.746	60
Tb	2881.31	10	U	2515.729	6
Ru	2881.276	30	V	2515.723	1
Rh I	2881.254	20	Bi I	2515.686	100
Ta	2881.232	30	Mo	2515.66	10
Cd I	2881.23	50R			
Ir	2881.158	15			
Th	2881.147	10			
Cr	2881.141	25			

SILVER (Ag)

Ionization Potential, 7.54 Volts

Most Sensitive Lines	Excitation Potential
3382.891 I	3.65 Volts
3280.683 I	3.75 Volts

Pr	3383.376	15
Ce	3383.279	8
Sb	3383.137	40
Th	3383.120	5
Yt	3383.05	3
Zr	3382.90	3
Er	3382.892	18
Ag	**3382.891**	**1000R**
Ce	3382.888	8
Yt	3382.83	3
Nd	3382.811	200
Tb	3382.80	15
Ce	3382.698	8
Cr II	3382.683	35
U	3382.675	4
Pr	3382.660	10
W	3382.606	10
Ce	3382.512	8
Mo	3382.484	15
Eu	3382.412	2h
Fe I	3382.409	50

U	3281.115	2
Ce	3281.095	18
Mo	3281.068	25
Th	3281.034	2
Os	3280.915	5
Yt II	3280.913	8
Ta	3280.872	3
Sm	3280.842	20
Mn	3280.756	60
Zr II	3280.748	3
Th	3280.736	2d
Cu	3280.685	10
Ag	**3280.683**	**2000R**
Co	3280.681	2
Mo	3280.671	3
Ce	3280.668	6
U	3280.608	1
Rh I	3280.55	30R
Lu	3280.50	10
Ce II	3280.485	15
U	3280.399	5
Ti	3280.391	3
Th	3280.374	10
Mo	3280.318	5
Tb	3280.28	30
Fe	3280.261	150

SODIUM (Na)

Ionization Potential, 5.12 Volts

Most Sensitive Lines	Excitation Potential
5895.923 I	2.09 Volts
5889.953 I	2.10 Volts
3302.988 I	3.74 Volts
3302.323 I	3.74 Volts

Yb	5896.61	5
Sm	5896.278	5
Na I	5895.923	5000R
Pb	5895.70	20hℓ
Tm	5895.626	80
Nd	5895.578	2
Fe	5895.497	4
Eu	5895.288	25
Co I	5890.484	7
Hf	5890.45	8
W	5890.333	7
Cr	5889.989	12
Mo	5889.978	50h
Na I	5889.953	9000R
Sm	5889.695	20
Tb	5889.06	10
Th	3303.487	5
Fe II	3303.471	5
U	3303.370	4
Mo	3303.342	25
W	3303.335	7
Cb	3303.320	1
Mn	3303.278	40
Ce II	3303.225	10
Re	3303.212	30
Mo	3303.113	4
La II	3303.11	400
Ir I	3303.091	3
Na I	3302.988	300R
Zn	3302.941	700R
Ca	3302.94	4
Ce	3302.913	10W
Cr	3302.876	30
Fe II	3302.859	1
U	3302.82	6
Ta	3302.765	50
Zr II	3302.666	10
Pr	3302.66	15
Tb	3302.64	8
Cb	3302.621	1
Zn I	3302.588	800
Bi	3302.55	150
U	3302.492	3
Dy	3302.472	4
Tm	3302.45	125
Yb	3302.44	7
Ta	3302.328	3
Na I	3302.323	600R
U	3302.26	1h
Re	3302.227	30
Cr	3302.19	50h
Cb	3302.176	5
Yt	3302.17	5
Pd I	3302.128	100wh
Pt	3302.12	2h
Ti II	3302.096	8
Sm	3302.092	8
Dy	3302.02	2
Eu	3301.95	25
Er	3301.93	15
Ru	3301.911	30
Ce	3301.905	10
Pr	3301.898	10
Ta	3301.895	25
Pt I	3301.861	300
W II	3301.85	1
Ir I	3301.757	2
U	3301.754	10
Sr I	3301.734	100

STRONTIUM (Sr)

Ionization Potential, 5.67 Volts

Most Sensitive Lines	Excitation Potential
4607.331 I	2.68 Volts
4077.714 II	3.03 Volts

Tb	4607.81	4	V I	4077.977	2
Fe I	4607.654	50	Dy	4077.974	150r
Mn	4607.625	50	Tb	4077.97	25
Nd	4607.381	25	Er	4077.970	20s
Au I	4607.34	30	Hg I	4077.811	150
Sr I	4607.331	1000R	U	4077.786	15
Co	4607.33	2h	Ta	4077.721	4
bh La	4607.3	3	Sn	4077.72	2
Ce	4607.290	3	Cu	4077.716	5
V	4607.226	4	Sr II	4077.714	400r
Ce	4607.087	2	Pr	4077.69	4
Mo	4607.075	8	Mo	4077.682	8
Pr	4606.920	3	Cr	4077.677	30
Ru	4606.833	4	Nd	4077.620	8
			Rh I	4077.57	5
Eu	4078.231	3	Ce II	4077.470	18
Pr	4078.16	5	Co I	4077.406	100wh
W	4078.124	7	Yt I	4077.366	50
Re	4078.124	10	Dy	4077.35	4
Mo	4078.074	4	La II	4077.340	600
Ho	4078.00	3	Yb	4077.27	30
Pr	4077.98	10	Ti I	4077.153	18

TANTALUM (Ta)

Ionization Potential, Volts

Most Sensitive Lines

3311.162
2714.674

Excitation Potential

Sc II	3311.708	3
Dy	3311.51	5
Ce	3311.497	15
Fe I	3311.453	1
Ce	3311.388	3
W	3311.382	15ℓ
U	3311.35	4d
Zr II	3311.339	8
Cb	3311.338	5
Cr I	3311.30	8
Ta	3311.162	300w
W	3311.112	5
Er	3311.09	3
Pd	3311.023	4
Ir I	3311.023	2
Cu I	3311.00	3
Dy	3310.96	5
Ru I	3310.957	30
Os	3310.912	200
Nd	3310.900	25
Ce	3310.877	10
U	3310.87	2d
Hf II	3310.856	15
Eu	3310.80	3wh
Tb	3310.80	8
Mo	3310.771	20
Sm II	3310.655	25
Fe	2715.125	5
Th	2715.092	6
Rh I	2715.045	50
V	2715.031	10
U	2714.998	6
Ce	2714.975	5
Fe I	2714.868	40
W	2714.815	4
Ce	2714.723	5
Ta	2714.674	200
Os	2714.642	50r
Th	2714.617	2h
U	2714.584	10
Ir I	2714.550	4
La I	2714.538	6
Co II	2714.418	12
Fe II	2714.412	200
Rh I	2714.410	150
U	2714.291	2
Zr II	2714.258	7
V	2714.199	60

TELLURIUM (Te)

Ionization Potential, Volts

Most Sensitive Lines	Excitation Potential
2385.76 I	5.8 Volts
2383.25 I	5.8 Volts
2142.75 I	5.8 Volts

Cr I	2386.19	20	Ir	2383.789	15	Os	2143.23	12
W	2386.17	8	Ta	2383.72	6	Cb	2143.21	4
Ir	2386.153	15	Tm	2383.67	15	V II	2143.047	10
Rh	2386.14	80	Pt I	2383.641	30	Re	2143.00	10
Os	2386.04	2	Sb	2383.63	75	Cb	2142.91	1h
Fe I	2385.95	4	W	2383.54	2h	Ir	2142.82	3
Ir	2385.863	20	Mo	2383.52	12	La	2142.81	2h
Co	2385.816	9	Re	2383.48	25	Re	2142.78	10
Te I	2385.76	600	Co II	2383.46	15	Te I	2142.75	600
Cr I	2385.74	25	Ir	2383.450	2	Os	2142.73	4
Ta	2385.73	8	V	2383.436	2	Pd	2142.57	3
Fe	2385.579	2	Rh	2383.40	50	Ta	2142.53	8h
U	2385.55	3	Cr I	2383.33	20	W	2142.511	3
Re	2385.50	12	Te I	2383.25	500	Pt II	2142.499	2
W II	2385.49	3	Fe II	2383.241	8	Os	2142.38	4
Os	2385.49	15	Os	2383.21	15	Rh	2142.28	3
Rh	2385.44	3	Ir	2383.168	10	Ir	2142.25	20
Ta	2385.35	2	Fe II	2383.055	6			
U	2385.28	2	V	2383.001	8			
			W	2382.986	15			
			Rh	2382.89	50			
			Dy	2382.85	2			
			Pd II	2382.756	2			

TERBIUM (Tb) *

Ionization Potential, Volts

Most Sensitive Lines

4326.48
4278.51

Excitation Potential

Ti I	4326.967	12	Pr	4278.99	15
U	4326.927	3	W	4278.93	4
Ce	4326.826	15	V	4278.883	2
Ru I	4326.825	20	Ce II	4278.866	20
Fe I	4326.760	10	Ti I	4278.813	25
Mn	4326.756	80	Ru	4278.689	7
Mo	4326.743	50	Mn	4278.676	15
U	4326.595	2	Pr	4278.62	10
Tb	4326.48	150	Dy	4278.61	3
Sr I	4326.445	8	Rh I	4278.598	25
Eu	4326.44	8w	Mo	4278.584	5
U	4326.426	2	Tb	4278.51	200
Yb	4326.40	20h	W	4278.410	10
Ho	4326.39	2	Th	4278.323	8
Dy	4326.39	2	Ce	4278.248	10
Ti I	4326.355	60	Ti I	4278.227	50
Cb	4326.327	30	Gd	4278.202	6
Gd	4326.291	3	U	4278.171	5
Os	4326.254	30	Pr	4278.04	35
Hf	4326.24	6h			
La I	4326.185	5			
Mo	4326.137	50			
Eu	4326.13	4w			
Sm	4326.127	2			
U	4325.897	10			

*See list of sensitive rare earth lines at end of tables.

THALLIUM (Tl)

Ionization Potential, 6.07 Volts

Most Sensitive Lines	Excitation Potential
5350.46 I	3.27 Volts
3775.72 I	3.27 Volts
3519.24 I	4.47 Volts

Ti I	5351.084	50
Cb	5351.045	3
Zr I	5350.899	2
Cb	5350.742	150
Sm	5350.618	15
Tl I	5350.46	5000R
W	5350.445	18
Er	5350.44	12
Gd	5350.406	25
Eu	5350.399	60h
Re	5350.392	2w
Zr II	5350.353	4
Sc I	5350.296	3
Zr II	5350.093	4
U	5349.917	5
V I	3776.157	50
Ce	3776.146	5
Mo	3776.104	5
Pr	3776.089	8
Sm	3776.06	15
Ti II	3776.059	8
Tb	3776.02	8
Dy	3776.01	2
Ba	3776.0	3
U	3775.991	10
Ce	3775.986	12
Th	3775.942	20
Fe I	3775.868	2
Ca	3775.86	2
Sm	3775.849	2
Bi	3775.745	2
Tl I	3775.72	3000
V I	3775.719	30
Rh I	3775.716	8
Eu	3775.69	4W
Er	3775.665	8
Mo	3775.647	15
U	3775.608	12
Ni I	3775.572	500h
Ce	3775.564	4
Nd	3775.501	10
Re	3775.464	10
Zr I	3775.461	7
Sm	3775.459	10
Cb	3775.448	5
W	3775.446	8
U	3775.442	4
Eu	3775.41	4W
Ce	3775.363	2
Th	3775.319	20
U	3775.262	6
Ni I	3519.766	500h
Tb	3519.76	50
Ce	2519.736	18
Th	3519.693	3d
Cb	3519.649	5
Ru	3519.635	70
Zr I	3519.605	100
Rh I	3519.541	40
Cr	3519.45	6h
Cb	3519.334	2
Tl I	3519.24	2000R
Bi	3519.18	10
Os	3519.176	15
V I	3519.167	10
Pr	3519.128	10
Er	3519.094	20rh
Ce	3519.077	25
Ru	3518.983	30
Tb	3518.96	15
U	3518.951	3
Os	3518.942	20
Ir I	3518.906	2h
Eu	3518.904	5
Th	3518.894	3d
Fe I	3518.882	10
Zr	3518.869	4
Hf II	3518.752	5

THORIUM (Th)

Ionization Potential, Volts

Most Sensitive Lines	Excitation Potential
4019.137 II	3.07 Volts
2837.299	

Pb	4019.639	6	Re	2837.549	40
Ru I	4019.553	12	Nd	2837.51	5
Dy	4019.48	5	Os	2837.422	25
Ce	4019.480	6	W	2837.344	12
Pr	4019.44	10	U	2837.328	10
Co I	4019.302	80	Ir I	2837.327	20
Ce II	4019.280	4	Mo	2837.320	5h
W	4019.231	18			
U	4019.203	6	Th	2837.299	15
Ce	4019.193	2	Sc	2837.293	4h
Co I	4019.140	5	Ce	2837.289	50s
			Ru	2837.274	20
Th II	4019.137	8	Zr I	2837.232	100
Re I	4019.130	15	Pt I	2837.230	2
Tb	4019.12	40	U	2837.187	10
Ni I	4019.046	5	Co I	2837.151	75r
Mo	4019.046	2	Er	2837.106	5
Ce	4019.044	15	Nd	2837.10	5
U	4018.990	25	Fe	2837.03	1
Ce	4018.919	2	Re	2837.015	2h
Nd	4018.826	15	Dy	2836.994	2h
Sm II	4018.539	4	Mo	2836.965	8
			Gd	2836.955	2
			In I	2836.919	80
W	2837.762	10	U	2836.918	5
U	2837.726	6	Cd I	2836.907	200
Dy	2837.613	2	Mo I	2836.705	1
Ce	2837.598	8	V I	2836.698	10

THULIUM (Tm)*

Ionization Potential, Volts

Most Sensitive Lines	Excitation Potential
3761.917 II	3.28 Volts
3761.333 II	3.28 Volts
3462.20 II	

Pr	3762.366	5	U	3761.601	2	Hf II	3462.641	15
Th	3762.363	10	Nd	3761.575	20	Ca	3462.62	2
Nd	3762.361	10	Ir I	3761.555	5	Er	3462.58	10
Tb	3762.34	3	Ru	3761.508	12	Tb	3462.51	8
Eu	3762.33	9w	Th	3761.475	10	Na II	3462.494	2
Ti	3762.305	10	Ce	3761.450	2	Ce	3462.433	8
Dy	3762.28	3	V I	3761.442	40	Fe I	3462.361	10
Ce	3762.280	4	Fe I	3761.408	20	Pr	3462.36	3
Ce	3762.220	3	Dy	3761.40	2h	La	3462.32	2
Gd	3762.212	10	Pr	3761.381	8	Ce	3462.234	3
Fe I	3762.209	7	Ta	3761.349	8	Eu	3462.21	5
Ir	3762.208	2	Tm II	3761.333	250	Tm II	3462.20	250
U	3762.114	10	Ti II	3761.323	100	Os	3462.191	20
Mo	3762.086	10	Ce	3761.185	3	Sc I	3462.183	4
Sr	3762.00	1	Sm	3761.144	6	Pr	3462.10	6
U	3761.961	2	Eu II	3761.134	10	Ru	3462.040	5
Ce	3761.953	2	Cb	3761.126	15	Rh I	3462.040	1000
Ir	3761.941	2	Tb	3761.12	15	Ho	3461.96	20
Tm II	3761.917	200	Th	3761.104	15	Gd	3461.956	5
Ti II	3761.888	12	U	3761.044	4	Ru	3461.924	30
Cr	3761.868	5h	Re	3761.025	2h	Pr	3461.873	6
Pr	3761.867	150	Yb	3761.00	3	W	3461.814	9
Mo	3761.755	6	Pr	3760.956	5			
Ca I	3761.72	2	Nd	3760.942	10d			
Cr	3761.701	4	Gd	3760.931	10			
W	3761.621	7	Mo	3760.885	6			
Pr	3761.606	10	U	3760.884	10			

*See list of sensitive rare earth lines at end of tables.

TIN (Sn)

Ionization Potential, 7.297 Volts

Most Sensitive Lines	Excitation Potential
3262.328 I	4.85 Volts
3175.019 I	4.31 Volts
2839.989 I	4.8 Volts

Ir I	3262.930	4
Er	3262.80	15
Re I	3262.765	25
Os	3262.751	100
Ir I	3262.718	3
Tb	3262.68	8
Th	3262.671	12
Mo	3262.628	15
Eu	3262.61	15
Sm	3262.579	3
Eu	3262.495	5
Hf	3262.474	10
Co	3262.435	2
Tb	3262.40	2
Pr	3262.39	2
Nd	3262.36	10d
Mo	3262.353	8
Pb	3262.353	20h
Sn I	3262.328	400h
Os I	3262.290	500R
Fe	3262.280	50
Ba I	3262.275	3
Dy	3262.27	2
Sm II	3262.263	10
Mo	3262.188	1
Ce	3262.138	5
V I	3262.062	10
Dy	3262.02	2
Fe	3262.013	30
Ir I	3262.010	20
Ba I	3261.96	40
Cb	3261.879	10
Mo	3261.84	2
Fe I	3175.447	200
U	3175.358	8
Ru	3175.298	30
Ru	3175.147	20
Te I	3175.11	30
Ce	3175.059	10
Mo	3175.049	2
Fe	3175.035	1
Sn I	3175.019	500h
Fe	3174.96	5
Co I	3174.905	80
Dy	3174.883	12
La II	3174.88	3
Ho	3174.86	6
U	3174.843	6
Pt I	3174.824	2
Re	3174.780	20w
Yb	3174.76	2
Mo	3174.672	4
Tb	3174.66	15
Mn	3174.651	15h
Re I	3174.619	30
V	3174.539	1
Fe I	2840.423	125
Ta	2840.39	2
Re I	2840.348	40
Gd	2840.236	50
W	2840.220	9
Ir I	2840.219	15
Ce	2840.156	3
Th	2840.156	8
V	2840.106	2
W	2840.097	9
Cr	2840.021	25
Mn	2840.001	20
Sn I	2839.989	300R
U	2839.890	18
Tm	2839.85	5
W II	2839.810	1
Cb	2839.80	2
Ta	2839.778	8
U	2839.651	5
Mo	2839.585	25
Ce	2839.561	5
Na II	2839.555	2
Fe II	2839.529	4

TITANIUM (Ti)

Ionization Potential, 6.81 Volts

*Most Sensitive Lines	Excitation Potential
4981.733 I	3.32 Volts
3998.640 I	3.13 Volts
3653.496 I	3.43 Volts
3349.406 II	3.73 Volts
3341.875 I, II	

Fe	4982.507	200
Yt II	4982.142	8
Ce	4982.132	8
Pr	4981.996	2
Dy	4981.96	2h
Ir	4981.879	3
Mo	4981.827	10
Ti I	4981.733	300
Sm II	4981.714	50
Re I	4981.541	15
Nd	4981.283	10
Th	4980.953	8
Ca	3999.13	2
Zr II	3998.968	30
Dy	3998.940	5h
Os	3998.933	80
Tb	3998.892	5
Cr	3998.860	25
Ir	3998.828	2
U	3998.820	3
Eu	3998.818	3W
W	3998.755	8
Ce	3998.750	2
V I	3998.730	100
U	3998.697	6
Pr	3998.690	4
Nd	3998.689	40
Ti I	3998.640	150
Cb	3998.444	2
Pr	3998.441	9
Tb	3998.404	7
Sm	3998.353	10
Mo	3998.286	8
Ho	3998.28	40
U	3998.242	5
Ce	3998.235	2
W	3998.159	7
Au	3653.93	5
Sr I	3653.928	15
Cr I	3653.912	100
Mo	3653.897	3
Tb	3653.87	15
Ta	3653.828	3
Fe I	3653.763	25
Ir I	3653.759	2h
Os	3653.725	30
Ce	3653.670	18
Pr	3653.653	4
Re I	3653.615	15
Cb	3653.615	10
Tm	3653.61	30
Yt	3653.606	5
Th	3653.59	3
Mo	3653.55	4d
W	3653.524	5
Ti I	3653.496	500
Au II	3653.491	3
Sm	3653.479	15
Ta	3653.393	3
W	3653.338	1
Ir I	3653.323	3
Sr I	3653.270	30
U	3653.209	10
Os	3653.201	10W
Ir	3653.191	15
Re	3653.161	4h
Nd	3653.150	10
Sm	3653.113	10
Ce	3653.108	15
Tb	3652.97	15
Re I	3349.910	20
Sm	3349.835	3
La I	3349.834	4
Fe	3349.738	1
W	3349.538	4
Co	3349.526	7
Cb	3349.523	30
U	3349.43	4d
Tb	3349.42	30
Ti II	3349.406	100
Ce	3349.405	4
Au	3349.40	15
Cb	3349.348	5
W	3349.340	2
Th	3349.340	5
Cr	3349.322	35
Cu I	3349.292	70
Co I	3349.222	3h
Sc I	3349.22	4
Mo	3349.193	6
Hf II	3349.17	5
Cr	3349.072	125
Cb	3349.059	80
U	3349.036	4
Ti II	3349.035	125
Th	3348.961	4
Ce	3342.312	3
Fe	3342.292	20
V	3342.28	5
Re I	3342.263	200
La I	3342.224	80
Fe I	3342.216	40
Ce	3342.195	3
Ti I	3342.151	12
Er	3342.11	7
Cr	3342.021	6
Cb	3341.974	100r
Co I	3341.947	25
Os	3341.914	10
Fe	3341.905	100
Eu	3341.892	5
Dy	3341.88	30
Ti I,II	3341.875	100
Ce I,II	3341.868	40
Mo	3341.846	8
Er	3341.836	18
Sm	3341.832	5
Ru	3341.664	70
U	3341.661	12
Ce	3341.640	2
Er	3341.61	12
Cb	3341.600	3
Ti I	3341.554	2
Hg I	3341.478	100
Pr	3341.473	10
Sm II	3341.435	5
Dy	3341.433	10

URANIUM (U)*

Ionization Potential, Volts

Most Sensitive Line 4241.669

Excitation Potential

Tm	4242.15	500	Na I	4241.6	3
Zr I	4242.013	4	Os	4241.521	9
Ce	4242.009	10	Co I	4241.514	3h
Hf II	4241.93	2	Cb	4241.449	3
Co I	4241.886	3h	W	4241.448	30
Dy	4241.83	2	Ce II	4241.405	5
Re I	4241.822	2	Re I	4241.387	30
Au I	4241.77	40	V I	4241.318	15
Ce	4241.743	3	Pr	4241.30	10
Pd I	4241.7	2h	Gd	4241.282	10
Zr I	4241.687	100	Ce	4241.244	3
U	4241.669	40	Nd	4241.208	12
Ce	4241.644	2	Zr I	4241.202	100

*Some other sensitive lines of uranium are: 4543.632, 4090.135 and 2882.741. At the time these wavelength tables were prepared, adequate information on the use of the most sensitive lines of uranium was not available. Recently several pertinent publications have appeared and the reader should consult the text for references to, and information on, the most sensitive lines of uranium.

VANADIUM (V)

Ionization Potential, 6.76 Volts

Most Sensitive Lines	Excitation Potential
4379.238 I	3.12 Volts
3185.396 I	3.94 Volts

Zr II	4379.776	10	Sm	3185.837	3
bh La	4379.7	20	Mo	3185.711	8
U	4379.644	2	U	3185.71	12
bh La	4379.6	10	Rh I	3185.593	100
Tb	4379.60	3w	Re I	3185.563	200
Pd I	4379.561	6	Eu	3185.56	10wh
Cb	4379.525	2	Ce	3185.506	2
Gd	4379.52	2	Tm	3185.48	20
Dy	4379.41	2	Ru I	3185.442	12
Bi II	4379.4	25	Ce	3185.413	4
Pr	4379.335	100w	U	3185.397	4
Yt I	4379.324	4	V I	3185.396	500R
Tb	4379.26	4	Os	3185.327	150
Ag	4379.25	5	Er	3185.247	15
V I	4379.238	200R	W	3185.202	6
Hf	4379.167	10h	U	3185.145	4
Ho	4379.15	3	Mo	3185.104	20
Nd	4379.111	2	Zr I	3185.075	2
Ce	4379.081	3	W II	3185.05	1
Pr	4378.836	3	Th	3184.898	10
Ta	4378.822	40	Ru I	3184.897	4
Ce	4378.818	4	Fe I	3184.896	200
Tb	4378.70	9w	Dy	3184.777	18

WOLFRAM (W)

Ionization Potential, Volts

Most Sensitive Lines	Excitation Potential
4302.108 I	3.23 Volts
4294.614 I	3.24 Volts
4008.753 I	3.44 Volts

Ce	4302.653	10
Dy	4302.57	2
U	4302.530	2
Ca I	4302.527	50
Yt I	4302.294	30
Fe I	4302.192	50
V I	4302.149	8
Bi II	4302.136	2h
W I	4302.108	60
Pr	4302.10	60
U	4302.089	5
Ti II	4301.934	25
Mo	4301.932	10
U	4301.723	6
Ho	4301.62	3
Er	4301.604	25

Th	4295.088	4
Er	4295.039	15
Dy	4295.038	20
Ho	4295.01	3
W	4295.005	5
Dy	4294.936	25
Zr I	4294.792	40
Ru I	4294.791	20
Hf	4294.787	25
Sc II	4294.767	20
Ce II	4294.756	10
Nd	4294.735	15
Pr	4294.700	25
Eu	4294.67	4
U	4294.651	3h
W I	4294.614	50
Mo	4294.599	6
Tb	4294.36	10
Fe I	4294.128	700
Ti II	4294.124	60

Pr	4009.24	5
Gd	4009.21	50
Tb	4009.193	5
U	4009.170	8
Er	4009.165	15
Th	4009.066	10
Ce	4009.063	12l
Ir I	4008.967	5
Ti I	4008.928	80
Gd	4008.922	20
U	4008.918	8
Fe	4008.873	5
Eu	4008.872	8w
Nd	4008.754	12
W I	4008.753	45
Pr	4008.714	150
U	4008.70	2
Ce	4008.664	8
Dy	4008.49	5
Hf II	4008.46	5

YTTERBIUM (Yb)*

Ionization Potential, 6.2 Volts

Most Sensitive Lines	Excitation Potential
3987.994 I	3.09 Volts
3694.203 II	3.34 Volts

La II	3988.518	1000
Ce	2988.518	8h
U	3988.293	2
Eu	3988.253	10W
Dy	3988.21	4
Os	3988.179	50
Cb	3988.157	5
U	3988.029	8
Pr	3988.019	25
Th	3988.015	50
W	3988.007	7
Yb I	3987.994	1000R
Ce	3987.990	5
Ho	3987.98	8
Er	3987.951	100r
Re	3987.929	3
Cr	3987.89	3
Gd	3987.842	50
Eu	3987.83	20w
Ir	3987.829	12
Nd	3987.810	25
Tb	3987.804	4
Ru	3987.795	3
U	3987.720	2
Th	3987.713	10
Ce	3987.699	2ℓ
Tb	3987.671	6
Er	3987.663	4
Ir I	3987.657	4
Ti	3987.610	8
Ho	3987.55	3
W	3987.524	5
Pr	3694.695	40
Cb	3694.666	10
V I	3694.622	60
Ag	3694.62	2h
Ta	3694.519	7h
W	3694.508	10
Ir	3694.454	2
Ti I	3694.447	80
Dy	3694.36	6
Th	3694.355	5
U	3694.325	6
Pr	3694.321	3
Sm	3694.314	15
La II	3694.27	4
Ho	3694.24	10
Yb II	3694.203	500R
Yt	3694.20	4
Er	3694.193	25d
Ce	3694.173	4w
Tb	3694.12	8
Mn	3694.115	5
Gd	3694.011	25
Fe I	3694.010	400
Sm II	3693.996	100
Th	3693.94	2
Ni I	3693.932	50
Dy	3693.84	4
Eu	3693.82	25w
Cb	3693.765	1
Ce I,II	3693.708	8

*See list of sensitive rare earth lines at end of tables.

YTTRIUM (Y)*

Ionization Potential, 6.5 Volts

Most Sensitive Lines	Excitation Potential
4374.935 II	3.23 Volts
3710.290 II	3.51 Volts
3242.280 II	3.99 Volts

Ti	4375.425	10
Cr	4375.333	25
Tb	4375.33	6
Dy	4375.33	10
V I	4375.304	20
Ce	4375.174	12
Sc I	4375.170	3
Ta	4375.143	15
Eu	4375.12	4
bh Zr	4375.1	8
Nd	4375.039	30
Mo	4375.014	8
Gd	4374.986	25
Sm II	4374.975	200
Mn	4374.947	150
Yt II	4374.935	150
Er	4374.925	40wh
Co I	4374.925	10
Nd	4374.923	20
Lu	4374.90	5
Mo	4374.888	8
Tb	4374.83	6
Ti II	4374.822	7
Rh I	4374.80	1000W
Dy	4374.80	12
Th	4374.790	15
Cb	4374.783	3
Ce	4374.760	3
Ca	4374.61	10
Sc II	4374.455	100
U	3710.785	4
Ho	3710.75	8
Dy	3710.73	4
Cr	3710.60	2
La II	3710.59	3
U	3710.534	3
Sb II	3710.519	2
Cb	3710.448	15
Ru	3710.316	4
Yb	3710.31	4
U	3710.308	8
Sm	3710.300	25
Er	3710.290	15wh
Yt II	3710.290	80
Eu	3710.29	20w
W	3710.289	4
Ce	3710.253	2
Ti I	3710.186	6
U	3710.168	1
Mo	3710.142	20
Cr	3710.09	4
Dy	3710.080	20
Pr	3710.012	6
Eu	3710.01	5
Ti I	3709.961	80
Re I	3709.937	40
Ce	3709.933	25
U	3709.878	2
Cb	3709.742	2
Zr I	3242.764	2h
Pd I	3242.703	2000wh
Ir I	3242.608	3
Ta	3242.566	7
Ce	3242.539	2
Cb	3242.531	3
Dy	3242.51	4
Sm II	3242.482	4
Nd	3242.455	4
Cb	3242.415	1
Ir I	3242.323	8
Dy	3242.285	4
Yt II	3242.280	60
Fe	3242.272	3
Th	3242.257	8
Ru	3242.165	80
Zr II	3242.163	1
Ce II	3242.135	12
Ta	3242.048	125
Sm	3242.031	40
W	3242.025	10
U	3241.991	10
Ti II	3241.986	60
Os	3241.982	15
Tb	3241.94	8
Be II	3241.835	5
Cb	3241.818	2
Os	3241.796	15

*See list of sensitive rare earth lines at end of tables.

ZINC (Zn)

Ionization Potential, 9.36 Volts

Most Sensitive Lines	Excitation Potential
4810.534 I	6.63 Volts
3345.020 I	7.75 Volts
2138.56 I	5.8 Volts

Mo	4811.062	50	Ru	3345.317	60	Ce	3344.552	4w
U	4810.889	6	Eu	3345.311	3	Yt	3344.55	3
Cr	4810.733	30	Ce	3345.230	3	Ru I	3344.532	60
Cb	4810.597	100	Cr	3345.15	15	Ca I	3344.513	100
Zn I	4810.534	400w	Ta	3345.108	3			
			W	3345.089	9			
Nd	4810.509	2	Nd	3345.088	12	Re	2139.15	18
Rh	4810.487	15	Sm	3345.02	1	Co I	2138.971	15
Ce	4810.392	6	Zn I	3345.020	800	Cb	2138.88	2
Dy	4810.241	2				Os	2138.75	3
Tb	4810.203	3r	Ti I	3344.931	8	Os	2138.61	8
Re	4810.104	4	W II	3344.904	3	Fe I	2138.589	8
Ru	4809.699	4	Th	3344.882	8	Ni I	2138.58	10
			U	3344.870	6	Ir	2138.57	15
			Ru	3344.797	5			
Zn I	3345.572	500	Zr II	3344.786	15	Zn I	2138.56	800R
U	3345.54	12	Ce II	3344.761	50			
Nd	3345.522	10	Pr	3344.758	2	Cb	2138.552	2
Er	3345.46	6	Er	3344.75	8	As	2138.53	2
Be I	3345.451	2	Mo	3344.746	50	Cu I	2138.507	25wh
Ce	3345.436	20	Ti I	3344.630	2	Os	2138.40	3
Dy	3345.37	3	Pr	3344.564	8	V II	2138.16	8
Cr	3345.37	18	U	3344.561	4	W II	2138.15	10
Mn	3345.352	15	La II	3344.560	300	Fe	2138.01	2

ZIRCONIUM (Zr)

Ionization Potential, 6.92 Volts

Most Sensitive Lines	Excitation Potential
4687.803 I	3.36 Volts
3438.230 II	3.68 Volts
3391.975 II	3.80 Volts

Hf	4688.39	30
Eu	4688.23	100
Ce	4688.229	2
Mo	4688.220	25
Ho	4688.20	2
Gd	4688.136	20
Sm	4688.132	4
Re	4687.858	15
Er	4687.835	3
Pr	4687.809	50
Zr I	4687.803	125
Cb	4687.781	5
W	4687.653	12
Ce	4687.637	2
Pr	4687.233	3
Yb	3438.72	4
Co I	3438.713	80W
U	3438.697	2
Os	3438.611	4
Tb	3438.57	15
Nd	3438.474	6
Er	3438.473	9
Hf	3438.432	12
Cb	3438.419	1
U	3438.407	3
Ru I	3438.368	70
Er	3438.32	12
Eu	3438.31	5
Pr	3438.31	25w
Fe	3438.306	10
Hf II	3438.235	25
Ce	3438.235	3
Zr II	3438.230	250
W	3438.210	7
Ir I	3438.094	6
Ce	3438.066	15
Sm II	3438.054	9
Yt	3437.953	3
Fe	3437.952	15
U	3437.934	6
V I	3437.873	2
Ce	3437.813	10
V I	3437.773	4
Ir	3392.475	2
Re	3392.384	3h
Cb	3392.338	20r
Fe I	3392.313	125
Ce	3392.256	3
Ti	3392.197	2
Mo	3392.173	15
Ho	3392.05	6
Th	3392.040	10
Cu I	3392.016	7
Fe	3392.014	20
Tb	3392.01	15
Eu	3391.992	40
Dy	3391.99	4
Er	3391.989	30
Zr II	3391.975	300
Nd	3391.948	6
Ru	3391.890	50
Ce	3391.884	3
Mo	3391.851	1
Sm	3391.841	2
Rh I	3391.73	3d
Tb	3391.72	15
Th	3391.717	1
Ce	3391.593	10
Cb	3391.591	1
Lu	3391.55	10
Mo	3391.536	4
W	3391.531	10
Cr II	3391.434	4

THE MOST SENSITIVE LINES OF THE RARE EARTH ELEMENTS

Wavelength	Intensity	Sensitivity	
		(M and S)	(S and W)
1. Cerium (Ce)			
4186.599 II	80	1	1
4137.646 II	25	3	3
4133.800 II	35	2	2
4040.762 II	70	5	4
4012.388 I, II	60	4	4
3942.151 II	35	-	4
3801.529 II	25	-	5
2. Dysprosium (Dy)			
4211.719 I	200	2	5
4186.810 I	100w	3	-
4045.983 I	150	4	-
4000.454 II	400	-	5
3968.395 II	300	5	-
3944.692 II	300	-	4
3645.416	300	-	2
3531.712	100	1	1
3407.80	150	-	3
3. Erbium (Er)			
4007.967 I	35	4	3
3906.316 II	25	5	3
3692.652	20	2	2
3499.104	18	3	3
3372.750	35	1	1
4. Europium (Eu)			
4205.046 II	200R	2	2
4129.737 II	150R	3	3
3971.99 I	1000R wh	5	5
3930.503 II	1000R	4	4
3819.66 II	500 wd	1	1
5. Gadolinium (Gd)			
3768.405	20	4	4
3646.196	200w	5	5
3422.466	80	1	1
3362.244	150	2	2
3350.482	150	3	3
6. Holmium (Ho)			
4103.84 I	400	4	3
4053.92 I	400	5	5
3891.02 II	200	2	2
3796.73	20	3	4
3456.00	60	1	1
3398.98	40	-	5

THE MOST SENSITIVE LINES OF THE RARE EARTH ELEMENTS (Cont'd)

Wavelength	Intensity	Sensitivity	
7. Lanthanum (La)		(M and S)	(S and W)
4086.714 II	500	3	5
3988.518 II	1000	2	2
3949.106 II	1000	1	1
3794.773 II	400	5	4
3790.822 II	400	4	3
8. Lutecium (Lu)			
3507.39 II	100	4	3
3397.07 II	50	-	-
3359.56 I	150	5	4
3077.60 II	100	3	5
2911.39 II	100	2	2
2615.42 II	100	1	1
9. Neodymium (Nd)			
4303.573 II	100	1	5
4156.083 II	10	4	4
4109.455 II	30	5	3
4061.085 II	40	3	2
4012.250 II	80	2	1
10. Praseodymium (Pr)			
4225.327 II	50	4	3
4222.98 II	125	5	5
4179.422 II	200	2	4
4100.746 II	200	3	2
3908.431 II	100	1	1
11. Samarium (Sm)			
3885.284 II	50	5	5
3634.271 II	100	4	3
3609.484 II	60	3	2
3592.595 II	40	2	1
3568.258 II	40	1	4
12. Terbium (Tb)			
3874.18 II	200	-	*
3676.35	100	3	
3585.03	15	2	
3561.74	200	4	
3509.17	200	1	
3324.40	70	5	

*No sample available.

THE MOST SENSITIVE LINES OF THE RARE EARTH ELEMENTS (Cont'd)

Wavelength	Intensity	Sensitivity	
13. Thulium (Tm)			
3848.018	400	2	*
3795.765	250	5	
3717.92	100	1	
3462.20	250	3	
3425.08	200	4	
3362.61	250	-	
14. Ytterbium (Yb)			
7699.49	2000	5	-
5556.476 I	1500	4	-
3987.994 I	1000R	3	3
3694.203 II	500R	1	2
3289.37 II	500R	2	1
15. Yttrium (Y)			
4374.935 II	150	2	5
4102.376 I	150	5	-
3774.332 II	12	3	2
3710.290 II	80	1	1
3600.734 II	100	4	3
3242.280 II	60	-	4

*No sample available

PERIODIC TABLE OF THE ELEMENTS

OUTER ELECTRONS ARE IN THE	I	II	III	IV	V	VI	VII	VIII	O
1st or K shell	1 H 1.0078								2 He 4.003
2nd or L shell	3 Li 6.940	4 Be 9.02	5 B 10.82	6 C 12.00	7 N 14.008	8 O 16.0000	9 F 19.00		10 Ne 20.183
3rd or M shell	11 Na 22.994	12 Mg 24.32	13 Al 26.97	14 Si 28.06	15 P 30.98	16 S 32.06	17 Cl 35.457		18 A 39.944
4th or N shell	19 K 39.096	20 Ca 40.08	21 Sc 45.10	22 Ti 47.90	23 V 50.95	24 Cr 52.01	25 Mn 54.93	26 Fe 55.85 27 Co 58.94 28 Ni 58.69	
	29 Cu 63.57	30 Zn 65.38	31 Ga 69.72	32 Ge 72.60	33 As 74.91	34 Se 78.96	35 Br 79.916		36 Kr 83.7
5th or O shell	37 Rb 85.48	38 Sr 87.63	39 Y 88.92	40 Zr 91.22	41 Nb 92.91	42 Mo 95.95	43 Tc	44 Ru 101.7 45 Rh 102.91 46 Pd 106.7	
	47 Ag 107.880	48 Cd 112.41	49 In 114.76	50 Sn 118.70	51 Sb 121.76	52 Te 127.61	53 I 126.92		54 Xe 131.3
6th or P shell	55 Cs 132.91	56 Ba 137.36	57 La 138.92 *	72 Hf 178.6	73 Ta 180.88	74 W 183.92	75 Re 186.31	76 Os 190.2 77 Ir 193.1 78 Pt 195.23	
	79 Au 197.2	80 Hg 200.61	81 Tl 204.39	82 Pb 207.21	83 Bi 209.00	84 Po 210	85 At 212.?		86 Rn 222
7th or R shell	87 Fr 223.?	88 Ra 226.05	89 Ac 227.05	90 Th 232.12	91 Pa 231.?	92 U 238.07	TRANSURANIC ELEMENTS 93 Np 94 Pu 95 Am 96 Cm		

* THE RARE EARTHS	58 Ce 140.13	59 Pr 140.92	60 Nd 144.27	61 Pm 146.0	62 Sm 150.43	63 Eu 152.0	64 Gd 156.9	65 Tb 159.2	66 Dy 162.46	67 Ho 164.94	68 Er 167.20	69 Tm 169.4	70 Yb 173.04	71 Lu 174.99

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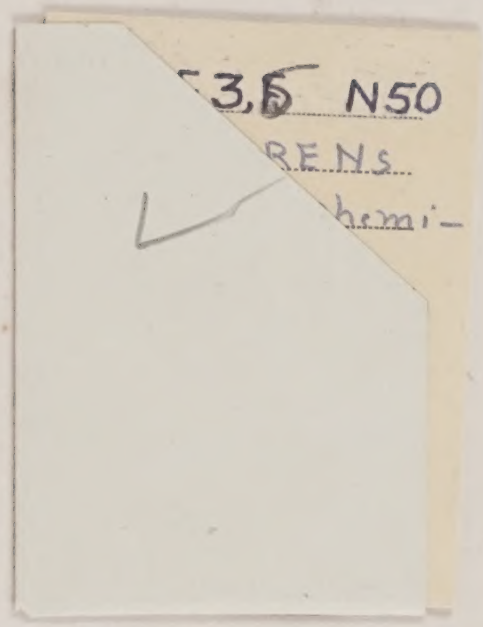
3,5 N50
RENs
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